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Control Techniques for Nitrogen Oxides Emissions from Stationary Sources
Second Edition

Acurex Corp, Mountain View, Calif Energy and Environmental Div

Prepared for

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16. ABSTRACT

This second edition of Control Techniques for Nitrogen Oxides Emissions from Stationary Sources (AP-67) presents recent developments of nitrogen oxides (NOx) control techniques which have become available since preparation of the first edition (published, March 1970). As required by Section 108 of the Clean Air Act, this second edition compiles the best available information on NOx emissions; achievable control levels and alternative methods of prevention and control of NOx emissions; alternative fuels, processes, and operating methods which reduce NOx emissions; cost of NOx control methods, installation, and operation; and the energy requirements and environmental impacts of the NOx emission control technology.

Each stationary source of NOx emissions is discussed along with the various control techniques and process modifications available to reduce NOx emissions. Various combinations of equipment process conditions and fuel types are identified and evaluated for NOx emission control.

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PREFACE

This document is the second edition of the EPA document entitled: Control Techniques for Nitrogen Oxides Emissions from Stationary Sources. This document was first published in 1970 as National Air Pollution Control Administration Publication No. AP-67. Some sections of the second edition have been substantially modified from the original, and others have required only minor updating. For example, Section 6 on NO_x control of nitric acid plants has been extensively rewritten. Additionally, Section 8 of the original edition, "Nitrogen Oxides Emission Factors" has been incorporated into Section 2. Section 9, "Possible New Technology" has been included in Section 3. This revision incorporates reviewers' comments from drafts of the second edition and adds new material on the energy and environmental impacts of the control techniques as required by Section 108 (b) (1) of the 1977 Clean Air Act.

The Energy and Environmental Division of Acurex Corporation has prepared this document for the Environmental Protection Agency. The EPA Project Officer was G. H. Wood, who was assisted by M. Davenport. The Acurex Program Manager was H. B. Mason and the Project Engineer was R. M. Evans; principal contributors were A. Balakrishnan, C. Castaldini, R. Schreiber, W. Toy, and L. R. Waterland.

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SUMMARY

In this document, the term "nitrogen oxides" or "NO_x" refers to either or both of two gaseous oxides of nitrogen, nitric oxide (NO), and nitrogen dioxide (NO_2). These substances are important in air pollution control because they are involved in photochemical reactions in the atmosphere and because, by themselves, they have harmful effects on public health and welfare.

CHARACTERIZATION OF NO_x EMISSIONS

Manmade oxides of nitrogen are currently emitted at a rate in excess of 20 Tg (22 million tons/yr) in the United States. Stationary sources account for approximately 60 percent of these emissions, of which 98 percent are due to combustion sources. Combustion generated NO_x is derived from two separate formative mechanisms, thermal NO_x and fuel NO_x. Thermal NO_x results from the thermal fixation of molecular nitrogen and oxygen in the combustion air. This is the dominant mechanism with the firing of clean fuels such as natural gas and distillate oil. Fuel NO_x results from the oxidation of organically bound fuel nitrogen compounds. This can be the dominant mechanism with the firing of coal and high nitrogen residual oils. The rate of formation of both thermal NO_x and fuel NO_x is strongly dependent on the combustion process conditions. The emissions due to both mechanisms are increased by intense combustion resulting from rapid mixing of the air and fuel streams. Additionally, the emissions due to thermal NO_x are sharply increased by increased local combustion temperatures.

Since equipment process conditions and fuel type are so important in determining NO_x emissions, the characterization of emissions and the evaluation of control potential requires detailed classification of stationary sources according to factors known to influence NO_x formation. Over 100 combinations of equipment type and fuel type are identified as having significantly different potential for NO_x emissions and/or NO_x control. The emission compilation for these sources for the year 1974 shows, however, that the 30 most significant equipment/fuel combinations are responsible for over 80 percent of stationary source emissions.

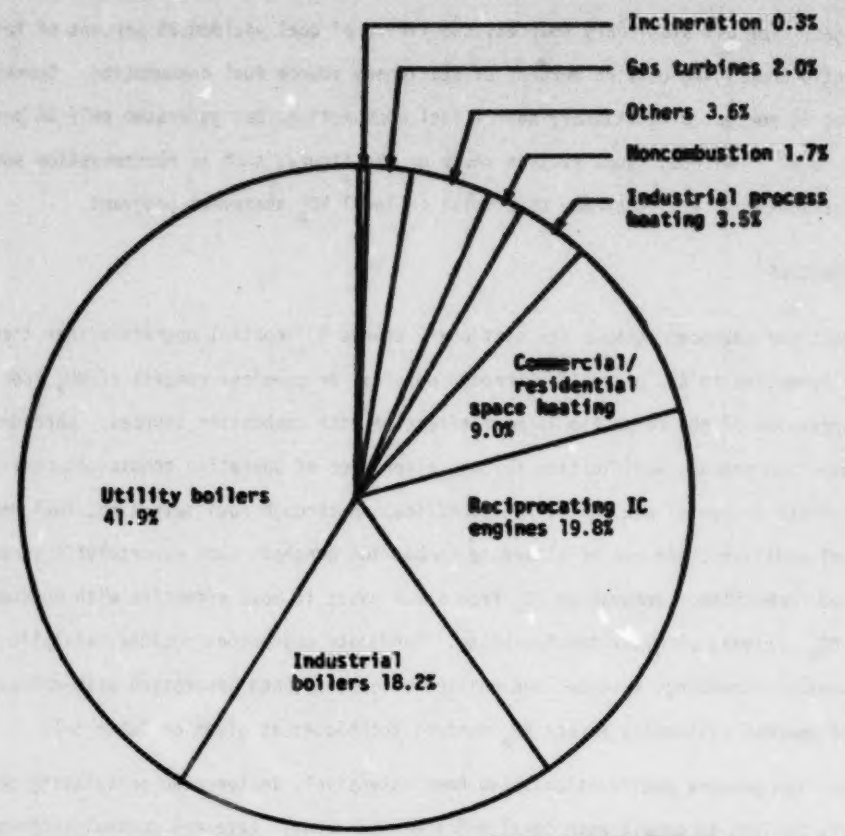
The total nationwide emissions in 1974 for stationary sources, grouped according to application sector, are shown on Figure S-1. On an uncontrolled basis, utility boilers accounted for over 40 percent of stationary source emissions. These boilers fired 61 percent coal, 18 percent oil, and 21 percent gas. For all stationary sources, the firing of coal yielded 35 percent of total NO_x emissions while comprising only 28 percent of stationary source fuel consumption. Conversely, natural gas comprised 42 percent of stationary source fuel consumption, but generated only 34 percent of stationary source NO_x. Although some sectors shown on the figure, such as noncombustion sources, are small on a nationwide scale, they may be crucial in local NO_x abatement programs.

CONTROL TECHNIQUES

Current and advanced methods for stationary source NO_x control operate either through suppression of NO_x formation in the process or through physical or chemical removal of NO_x from the stack gases. Suppression of NO_x formation is most effective with combustion sources. Candidate approaches include combustion process modification through alteration of operating conditions on existing systems or alternate design of new units, fuel modification through fuel switching, fuel denitrification, or fuel additives, and use of alternate combustion concepts such as catalytic combustion and fluidized bed combustion. Removal of NO_x from stack gases is most effective with noncombustion sources of NO_x, chiefly chemical manufacturing. Candidate approaches include catalytic reduction, with wet chemical scrubbing, extended and chilled absorption, and adsorption with molecular sieves. A summary of general stationary source NO_x control techniques is given on Table S-1.

Combustion process modifications have been extensively implemented on existing gas and oil fired utility boilers to comply with local emission standards. External control techniques such as low excess air firing, biased burner firing, overfire air and flue gas recirculation have yielded emission reductions up to 60 percent of uncontrolled, baseline operation. A summary of combustion modification concepts is given in Table S-2.

With coal firing, the most effective combustion modification technique for utility boilers is a combination of low excess air firing and off-stoichiometric combustion through biased firing, overfire air, or use of delayed mixing burners. Utility boiler manufacturers are currently including these procedures in new unit designs to comply with the Standard of Performance for New Stationary Sources of 301 ng/J (0.7 lb $NO_2/10^6$ Btu). Retrofit implementation of low excess air and off-stoichiometric combustion has shown that a level of 258 ng/J (0.6 lb $NO_2/10^6$ Btu) is achievable with some unit designs. Emission levels as low as 189 ng/J (0.44 lb $NO_2/10^6$ Btu) have been demonstrated on a tangentially fired unit equipped with factory installed overfire air. Current



Source	Estimated NO_x Emissions Tg	10^6 Tons
Utility Boilers	5.105	5.628
Industrial Boilers	2.218	2.444
Reciprocating IC Engines	2.413	2.660
Commercial/Residential Heating	1.090	1.202
Industrial Process Heating	0.432	0.476
Noncombustion	0.203	0.224
Gas Turbines	0.236	0.260
Incineration	0.039	0.043
Other	0.435	0.479
TOTAL	12.171	13.416

Figure S-1. Summary of 1974 stationary source NO_x emissions.

TABLE S-1. SUMMARY OF NO_X CONTROL TECHNIQUES

Technique	Principle of Operation	Status of Development	Limitations	Applications	
				Near-Term	Long-Term
Combustion Modification	Suppress thermal NO_x through reduced flame temperature, reduced O_2 level; suppress fuel NO_x through delaying fuel/air mixing or reduced O_2 level in primary flame zone	Operational for point sources; pilot-scale and full scale studies on combined modifications, operational problems and advanced design concepts for area sources	Degree of control limited by operational problems	Retrofit utility, industrial boilers, gas turbines; improved designs; new utility boilers.	Optimized design area, point sources
Flue Gas/ Noncombustion Tail Gas Treatment	Additional absorption of NO_x to HNO_3; conversion of NO_x to NH_4NO_3; reduction of NO_x to N_2 by catalytic treatment	Operational for existing and new nitric acid plants meeting NSPS; pilot scale feasibility studies for conventional combustion systems	New wet processes developing experience in applications; old catalytic processes have high costs interference by fuel sulfur or metallic compounds	Noncombustion sources (nitric acid plants)	Possible supplement to combustion modifications; simultaneous SO_x/NO_x removal
Fuel Switching	Simultaneous SO_x and NO_x control by conversion to clean fuels; synthetic gas or oil from coal; SRC; methanol; hydrogen	Synthetic fuel plants in pilot-scale stage; commercial plants due by mid-1980's	Fuel cost differential may exceed NO_x, SO_x, control costs with coal	Negligible use	New point sources, (combined cycle) Convert area sources (residential)
Fuel Additives	Reduce or suppress NO by catalytic action of fuel additives	Inactive; preliminary screening studies indicated poor effectiveness	Large make-up rate of additive for significant effect; presence of additive as pollutant	Negligible use	Not promising
Fuel Denitrification	Removal of fuel nitrogen compounds by pretreatment	Oil desulfurization yields partial denitrification	Effectiveness for coal doubtful; no effect on thermal NO_x	Negligible use	Supplement to combustion modification
Catalytic Combustion	Heterogeneously catalyzed reactions yield low combustion temperature, low thermal NO_x	Pilot-scale test beds for catalyst screening, feasibility studies	Limited retrofit applications; requires clean fuels	Small space heaters	Possible use for residential heating, small boilers, gas turbines
Fluidized Bed Combustion	Coal combustion in solid bed yields low temperature, low NO_x	Pilot-scale study of atmospheric and pressurized systems; focus on sulfur retention devices	Fuel nitrogen conversion may require control (staging); may require large make-up of limestone sulfur absorbent	Negligible use	Utility, industrial boilers beginning 1980's; possible combined cycle, waste fuel application

TABLE S-2. SUMMARY OF COMBUSTION PROCESS MODIFICATION CONCEPTS

Combustion Conditions	Control Concept	Applicable Equipment	Effect on Thermal NO_x	Effect on Fuel NO_x	Primary Applicable Controls		
					Operational Adjustments	Hardware Modification	Major Redesign
Decrease primary flame zone O_2 level	Decrease overall O_2 level	Boilers, furnaces	Reduces O_2-rich, high-NO_x pockets in the flame	Reduces exposure of fuel nitrogen intermediaries to O_2	Low excess air firing	Flue gas recirculation (FGR)	
	Delayed mixing of fuel and air	Boiler, furnaces	Flame cooling and dilution during delayed mix reduces peak temp.	Volatile fuel N reduces to N_2 in the absence of oxygen	Burner adjustments	Low-NO_x burners	Optimum burner/firebox design
	Increased fuel/air mixing	Gas turbines	Reduces local hot stoichiometric regions in overall fuel lean combustion	Increases	Improved atomization		New can design; premix, prevap.
	Primary fuel-rich flame zone	Boilers, furnaces, IC engines	Flame cooling in low-O_2, low-temp. primary zone reduces peak temp.	Volatile fuel N reduces to N_2 in the absence of oxygen	Burners out of service; biased burner firing	Overfire air ports, stratified charge	Burner/firebox design for two-stage combustion
Decrease peak flame temperature	Decrease adiabatic flame temperature	Boilers, furnaces, IC engines, gas turbines	Direct suppression of thermal NO_x mechanism	Ineffective	Reduced air preheat	Water injection, FGR	
	Decrease combustion intensity	Boilers, furnaces	Increased flame zone cooling yields lower peak temp.	Minor direct effect; indirect effect on mixing	Load reduction		Enlarged firebox, increased burner spacing
	Increased flame zone cooling/reduce residence time	Boilers, furnaces	Increased flame zone cooling yields lower peak temp.	Ineffective	Burner tilt		Redesign heat transfer surfaces, firebox aerodynamics
Chemically reduce NO_x in post-flame region	Inject reducing agent	Boilers, furnaces	Decomposition	Decomposition		Ammonia injection possible on some units	Redesign convective section for NH_3 injection

developmental activity is focusing on identifying and, if required, correlating operational problems, such as increased waterwall corrosion with boiler tubes of conventional chemical composition when exposed to the reducing conditions at the surface resulting from combustion modifications.

Retrofit combustion process modifications have also been extensively applied to gas turbines. Water injection has been successfully implemented to achieve emission levels of 75 ppm at 15 percent excess oxygen. Current activity is focusing on development of dry controls using premixing, prevaporization and controlled mixing for application to new combustor can designs.

There has been only limited field implementation of combustion process modification for other stationary combustion equipment e.g., industrial and commercial boilers, residential and commercial space heating equipment, reciprocating internal combustion engines and industrial process furnaces. The following sequence is being pursued for NO_x control development for these sources: control from operational fine tuning (e.g., low excess air firing, burner tuning), minor retrofit modifications (e.g., biased burner firing), extensive hardware changes (e.g., new burners) and major new equipment redesign (e.g., optimized heat transfer surfaces and burner aerodynamics).

Fuel switching for NO_x control is not currently practiced due to the supply shortage of clean fuels. A number of alternate fuels such as methanol and low-heating-value gas have low NO_x-forming potential and may be utilized in the 1980's. The economic incentive for alternate fuel use usually depends on factors other than NO_x control, e.g., desulfurization cost tradeoffs, system efficiency.

Fuel oil denitrification, usually as an adjunct to oil desulfurization, shows promise for reducing fuel NO_x. This concept may be effective for augmenting combustion modifications for NO_x control with the firing of residual oil. Fuel additives are not directly effective for suppressing NO_x emissions. Their use to suppress fouling and smoke emissions, however, may permit more extensive use of combustion control methods than would otherwise be practical.

Alternate combustion concepts under development include catalytic combustion and fluidized bed combustion. Lab-scale tests of catalytic combustion have demonstrated extremely low NO_x emissions with clean fuels (1-5 ppm). This concept may see application in the 1980's to stationary gas turbines and space heating systems. Fluidized bed combustion pilot plants have demonstrated NO_x emissions of the same order as conventional coal-fired power plants using process modifications for NO_x control (170 ng/J, or, 0.4 lb $NO_2/10^6$ Btu). The potential for replacement of conventional utility and industrial boilers by FBC depends on a number of other factors such as SO_x control cost tradeoffs and operational flexibility, e.g., load following.

Stack gas treatment for NO_x removal has been implemented in the U.S. only on noncombustion sources. Here, an additional incentive is the recovery of NO_2 as a feedstock material. The most widely tested technique is catalytic reduction with selective or nonselective reducing agents. The short supply of reducing agents (methane, ammonia) coupled with the loss of tail gas NO_2 as a potential feedstock is causing interest to shift to alternate processes such as molecular sieve absorption and extended absorption.

Flue gas treatment (FGT) of combustion sources has been at a low level of development in the U.S. due largely to the lack of regulatory incentive. The developmental activity has recently accelerated, however, as a result of increased emphasis on stationary source NO_x controls in the national NO_x abatement program. Flue gas treatment could be effective in the 1980's to augment combustion process modifications on large sources if stringent emission control is required, for example, to comply with a potential short-term NO_2 air quality standard. Current developmental activity includes transferring FGT technology from Japan where stringent NO_x controls are enforced. Processes being considered include selective catalytic reduction, selective homogeneous reduction and wet scrubbing. The dry systems show most promise for NO_x removal alone. For simultaneous NO_x/SO_x removal, several wet and dry processes are effective but the cost tradeoffs have not been identified.

A summary evaluation of NO_x control techniques for combustion sources is given in Table S-3.

LARGE FOSSIL FUEL COMBUSTION PROCESSES

The three largest stationary emitters of NO_x are electric power plant boilers (42 percent of the total), industrial boilers (18 percent) and prime movers, such as gas turbines and I.C. engines (20 percent). The most successful NO_x reduction technique is modification of operating conditions. For utility boilers, techniques such as lowering excess air, off-stoichiometric combustion, and, for gas- ans oil-fired units, flue gas recirculation have resulted in NO_x reductions of up to 60 percent making it possible for them to meet emissions regulations at costs of $1 to $10 per kW (electric output). Ongoing performance tests are investigating potential side effects of the modifications, such as increased corrosion and particulate emissions with coal firing.

Although less well developed for industrial boilers, some combustion modifications for these sources are able to decrease NO_x by up to 50 percent with no efficiency impairment or increase in particulate formation. The most successful techniques are lowering excess air, staged combustion, and flue gas recirculation.

The energy impacts of applying combustion modification NO_x controls to utility and industrial boilers occur largely through the effects on unit fuel-to-steam efficiency. This is usually

TABLE S-3. OVERALL EVALUATION OF NO_x CONTROL TECHNIQUES FOR COMBUSTION SOURCES

Control Technique	Existing Applications	Effectiveness	Operational Impact	Projected Applications	Control Evaluation
Low excess air (LEA)	Retrofit and new utility boilers; some use in industrial boilers	10% to 30% for thermal and fuel NO_x	Increase in efficiency; amount limited by smoke or CO at very low EA	Widespread use for efficiency increase; incorporate into advanced designs all sources	Primary emphasis near-term and far-term applications (all sources); combined with OSC & burner mods for far-term appl.
Flue gas recirculation (FGR)	Retrofit use on many gas- and oil-fired utility boilers; demonstrated on industrial boilers	20% to 50% for thermal NO_x; no effect on fuel NO_x	Possible flame instability; increased vibration	Possible use in new industrial boiler designs	Primary emphasis near-term applications large boilers; possible far-term industrial boiler application
Off-stoichiometric combustion (OSC) incl. OFA, BOOS, BBF	New and retrofit use on many utility boilers; demonstrated on industrial boilers	20% to 50% for thermal and fuel NO_x	No major impact with new design; potential for flame instability, efficiency decrease, increased corrosion (coal-fired) with retrofit	Widespread use in large boilers; incorporate into advanced designs	Primary emphasis near-term and far-term applications all sources
Load reduction	Some retrofit use on gas and oil utility boilers; enlarged fireboxes on new coal units	0% to 40% for thermal NO_x	Decrease in efficiency and power output; limited by spare capacity and smoke formation	Enlarged fireboxes used in new unit design; limited use for retrofit	Secondary emphasis near-term applications (boilers); combined with OSC or burner mods for far-term appl.
Burner modifications	New and retrofit use on utility boilers; demonstrated on residential furnaces	30% to 60% for thermal and fuel NO_x	No major impact with new design; retrofit use constrained by firebox characteristics	Incorporate into advanced designs utility, industrial boilers, residential, process furnaces, GT; combine with OSC	Primary emphasis near- and far-term applications all sources

TABLE S-3. OVERALL EVALUATION OF NO_x CONTROL TECHNIQUES FOR COMBUSTION SOURCES (Continued)

Control Technique	Existing Applications	Effectiveness	Operational Impact	Projected Applications	Control Evaluation
Water, steam injection	Widely used for gas turbines	30% to 70% for thermal NO_x	Slight decrease in efficiency; limited by CO formation; power output increases	Use in new gas turbines; possible use in process furnaces	Primary emphasis near-term applications, gas turbines; possible far-term industrial process application
Reduced air preheat (RAP)	Widespread use in large turbocharged IC engines	10% to 40% for thermal NO_x	Slight decrease in efficiency, increase power output	Continued use in IC engines	Secondary emphasis
Ammonia injection	Demonstrated on oil- and gas-fired industrial boilers	40% to 70% for thermal and fuel NO_x	Retrofit use limited; possible adverse environmental impact	Use in large boilers in some areas (1980's)	Primary emphasis far-term application to large boilers; evaluate impact with coal firing
Fuel denitrification	Oil denitrification accompanies desulfurization for some large boilers	10% to 40% for fuel NO_x	No adverse effects	Use of oil denitrification in large boilers as supplement to CM tech.	Secondary emphasis; evaluate as alternate fuel
Fuel additives	Fuel additives for NO_x not used	Generally ineffective for direct NO_x reduction	Byproduct emissions formed	Additives for corrosion, fouling, particulate, smoke, etc. can provide increased flexibility with CM tech. on large boilers	Secondary emphasis; consider impact of additives
Alternate and mixed fuels	Combustion of low nitrogen alternate fuels being demonstrated	Varies	Varies	Combined cycles and residential and commercial heating systems	Secondary emphasis far-term application; evaluate differential impact of fuel switching; transfer results of other E/A's .

TABLE S-3. OVERALL EVALUATION OF NO_x CONTROL TECHNIQUES FOR COMBUSTION SOURCES (Continued)

Control Technique	Existing Applications	Effectiveness	Operational Impact	Projected Applications	Control Evaluation
Catalytic combustion	Only tested in experimental combustors	>90% for thermal NO_x	Requires clean fuel; combustors limited by catalyst bed temp. capability	Gas turbines and residential and commercial heating systems	Primary emphasis far-term applications; compare impact to burner mods, alternate fuels
Fluidized bed combustion	Tested in pilot/prototype combustors	20% to 50% for fuel NO_x (pressurized FBC)	Requires sulfur acceptor	Combined cycle, utility boilers, industrial boilers (1980's)	Transfer results from FBC E/A; compare impact to combustion modifications, conventional combustion
Flue gas treatment (FGT)	Used in Japan on large boilers	40% to >90% for fuel and thermal NO_x	Requires temp. controls, catalyst, scrubbing soln., or oxidizing agent; possible adverse environmental impact	Possible supplement to CM for utility and large industrial boilers (1980's)	Secondary emphasis; transfer results of other studies to compare impact to combustion mods

expressed as an increase or decrease in fuel consumption for a constant output. Generally, flue gas recirculation and off-stoichiometric combustion have very little effect on efficiency. In some cases, taking burners out of service may result in reduced capacity. Low excess air and reduced air preheat have a slight impact, usually less than 1.5 percent increase in fuel use; although, significant reductions in air preheat (~ 150-200K) can have a much greater impact (~ 3-4 percent increase in fuel use). New designs should significantly reduce any adverse efficiency impacts.

Emissions of other pollutants, CO, HC, particulates, sulfates, and organics, can be altered by the use of NO_x control. Generally, these changes have been acceptable. In some cases specific consideration of other emissions has been given in the design or method of application of the NO_x control technique.

Prime movers include stationary reciprocating internal combustion engines and gas turbines. For the former, "dry" methods such as spark retard, air/fuel ratio change, and derating work well, providing NO_x reductions of 10 to 40 percent while fuel consumption increases 2 to 15 percent. Water injection ("wet" control) is currently the most effective technique for gas turbines, reducing NO_x up to 90 percent at costs of 0.4 to 14 mills/kWh, depending on the turbine's application. "Dry" control techniques show potential, but it will be a number of years before their development will be complete and they will be ready to be applied to large production turbines.

The energy impacts of applying NO_x control to internal combustion engines and gas turbines are manifested almost exclusively through corresponding increases in fuel consumption. Since both types fire mainly clean fuels, the impact on other emissions is confined primarily to HC, CO, and particulates (smoke).

OTHER COMBUSTION PROCESSES

Space heating, incineration and open burning, and industrial process heating are additional combustion sources of NO_x. Residential and commercial space heating contributes 9 percent of the nation's stationary NO_x emissions. Emissions of CO and smoke from the major equipment types, residential and commercial warm air furnaces, can be controlled by burner maintenance, tuning, or replacement. These techniques are ineffective for NO_x reduction, however. The most promising prospect for NO_x control in space heating systems is for new equipment applications. New low NO_x systems are available at a cost of 10 percent or more above conventional systems. These systems are capable of reducing NO_x emissions by more than 50 percent, while increasing operating efficiency by more than 5 percent.

There has been negligible application of combustion modification to incineration and open burning and to industrial process heating equipment.

NONCOMBUSTION PROCESSES

Noncombustion-generated NO_x, only 1.7 percent of stationary emissions, is produced mainly during nitric acid manufacture. NO_x control methods include extended absorption, wet scrubbing, and catalytic reduction. Catalytic reduction was initially practiced but because of catalyst costs, fuel costs and changes in the operating conditions of nitric acid plants, greater use of the extended absorption and wet scrubbing processes have been employed more recently. Other minor noncombustion sources are mainly those that use nitric acid as a feedstock. Control methods are similar to those used for nitric acid manufacturing. Table S-4 gives a summary of tail gas abatement processes and applications.

TABLE S-4. NO_x ABATEMENT METHODS ON NEW OR EXISTING NITRIC ACID PLANTS

Process	Method	Comments	Licensors	Examples
Chilled Absorption	Increased solubility of NO_x in chilled water	Usually cannot meet NSPS without other add-on technology or lowered acid product concentration	COL-VITOK	2-318 Mg/d (350 tons/day) (with Gulf catalytic reduction add-on). Nitram, Tampa, Fla.
			TVA	2-50 Mg/d (55 tons/day) plants at Muscle Shoals, (1972)
Extended Absorption	Increased absorption of NO_x by additional absorption equipment	Inlet pressure of 760 kPa required (additional compressors may be required)	J. F. Pritchard (Grande Paroisse)	327 Mg/d (360 tons/day) plant, Miss. Chemicals, Yazoo City, Miss. 1973. 272 Mg/d (300 tons/day) Holston Army Ammunition Plant, Kingsport, Tenn. Cominco Plant, Beatrice Neb. Kaiser, Tampa, Fla. and Bainbridge, Ohio
			P. M. Weatherly	9 U.S. plants, 1 Japan plant (employs chilled absorption process)
			Chemico	908 Mg/d (1000 tons/day) Monsanto, Pensacola, Fla. 1977.
		Requires additional compressor	Uhde	250 Mg/d (275 tons/day) plant, Allied Chemical, Omah, Neb. 1975
			C&I Girdler CoFAZ	None built to date
Wet Chemical Scrubbing	Scrubbing tail gases with urea solution or ammonia to recover NO_x	Performs better at high pressure but operable at lower pressures. Recovers ammonium nitrate and urea solution. Requires refrigeration.	MASAR (urea scrubbing)	Ill. Nitrogen Plt., Marsalles, Ill. Air Products & Chem., Pace, Fla.
			Norsk Hydro (urea scrubbing)	Norsk Hydro, Proggunn, Norway
		May require an evaporator to produce a concentrated ammonium nitrate by product. No refrigeration required.	Goodpasture (ammonia scrubbing)	90 Mg/d (100 tons/day) Goodpasture plt., 1974. Dimmitt, Texas Chevron Oil Co., Richmond, Calif. 1976 C.F. Industries, Fremont, N.D. 2 scrubbers for 7 plants totalling 544 mg/d (600 tons/day). Cyanamid, Welland, Ont.

TABLE S-4. NO_x ABATEMENT METHODS ON NEW OR EXISTING NITRIC ACID PLANTS (Concluded)

Process	Method	Comments	Licensors	Examples
Catalytic Nonselective	Burns NO_x and O_2 with CH_4 or H_2 to form N_2, H_2O, CO_2	• Consumes natural gas, uneconomical if high NO_x or O_2 content (also reacts with O_2) • May be used in conjunction with extended absorption • Energy recovery possible • Works at low or high pressure	C&I Girdler	Olin, Lake Charles, La. (also, Weatherby plants)
			D. M. Weatherly	IMC Corp., Strelington, La. (1976) (with extended absorption). 817 Mg/d (900 tons/day), 1977. Columbia Nitrogen, Augusta, Ga.
			Chemico	Location not available
Catalytic Selective	Burns NO_x with ammonia to form N_2 and H_2O; O_2 not affected	• Uses ammonia, can be expensive to operate • Often used with extended absorption • Works at low or high pressure • Energy recovery usually not possible • Can achieve very low emission if desired	Gulf	Nitram plants in Tampa, Fla., installed after CDL/VITOK process. 10 plants in U.S.
			Uhde (BASF catalysts)	Plants in Europe and Japan
			Mitsubishi	
Heterogeneous Catalysis	Oxidation of NO → NO_2 catalyzed by heterogeneous catalysis before absorption	Limited success	CDL/VITOK	Under development
Chemical Absorption	Oxidation with $KMnO_4$ ($KMnO_4$ electrolytically reclaimed	Uneconomical not presently offered	Carus Chemical	2 plants in Japan, not currently offered in U.S.
Molecular Sieve	Absorption by molecular sieve, regeneration of the sieve by thermal cycling	• High energy and capital demands • Hard to fit cycling of sieve into continuous plant operation	Purasiv N (Union Carbide)	50 mg/d (55 tons/day) Hercules, Inc. Bersemer, Ala. 1974 50 mg/d (55 tons/day) U.S. Army, Holston, Kingston, Tenn. (inoperable, dismantled)

SECTION 1

INTRODUCTION

Manmade oxides of nitrogen (NO_x) are currently emitted at a rate in excess of 20 Tg (22 million tons) per year in the United States. Over 98 percent of manmade NO_x emissions result from combustion with the majority due to stationary sources. Combustion generated oxides of nitrogen are emitted predominantly as nitric oxide, NO, a relatively harmless gas, but one which is rapidly converted in the atmosphere to the toxic nitrogen dioxide, NO_2. Nitrogen dioxide is deleterious to human respiratory functions and, with sustained exposure, can promote an increased incidence of respiratory ailments. Additionally, NO_2 is an important constituent in the chemistry of photochemical smog. The NO/NO_2 conversion in the atmosphere promotes the formation of the oxidant ozone, O_3, which subsequently combines with airborne hydrocarbons to form the irritant peroxyacetylnitrates (PAN). Nitrogen dioxide is also a precursor in the formation of nitrate aerosols and nitrosamines, the health effects of which are under study by the EPA. Because of the quantity generated and their potential for widespread adverse effects on public health and welfare, nitrogen oxides are among the atmospheric pollutants for which standards and regulatory controls have been established both by the U.S. Environmental Protection Agency (EPA) and by State and local agencies.

As part of the regulatory control program, the U.S. Environmental Protection Agency (nee the National Air Pollution Control Administration) published "Control Techniques for Nitrogen Oxide Emissions from Stationary Sources" (AP-67) in March 1970, as one of a series of documents summarizing technology for the control of air pollutants. Since the issuance of AP-67, there has been considerable activity in both regulatory control of NO_x and development of emission control techniques for stationary sources. Under provisions of the 1970 Clean Air Act Amendments, the EPA promulgated, in 1971, a National Ambient Air Quality Standard for NO_2 of 100 $\mu g/m^3$ annual average. To achieve and maintain this standard, a number of State and local agencies have established NO_x emission control standards for new and existing large stationary combustion sources and nitric acid plants. Additionally, Standards of Performance for New Stationary Sources were promulgated by the EPA in 1971 for steam generators with thermal input greater than 73.2 MW (250×10^6 Btu/hr) and nitric acid plants. Standards of performance for stationary gas turbines were proposed on October 3, 1977.

Standards for stationary large bore reciprocating engines are in preparation. The standard for large steam generators is under review to determine if additional stringency is appropriate.

The NO_x control technology development to support the implementation of these standards has shown widespread advancement since the publication of the AP-67 document. Efforts have proceeded on methods which suppress NO_x formation, through combustion process modification, and on methods which remove NO_x from the flue or tail gases, through stack gas treatment.

Combustion process modification is the preferred method for control of stationary combustion sources accounting for 98 percent of stationary source NO_x. Process modifications have been extensively applied to retrofit of existing utility and industrial boilers and gas turbines firing gas and oil. The significant role of fuel bound nitrogen in NO_x formation with the firing of coal and heavy oils was shown early in the control development effort. Current activity is concentrating on refinement of fuel NO_x control methods for application to advanced designs of coal-fired combustion equipment. Progress has also been made in the design of low-NO_x residential and commercial space heating systems.

Stack gas treatment is the preferred method for control of NO_x emissions from stationary noncombustion sources. These sources, primarily nitric acid plants, contribute less than 2 percent of nationwide stationary sources NO_x emissions, but can present a serious local hazard. Several control techniques, including extended absorption, catalytic reduction, wet scrubbing, and molecular sieve absorption, have been developed and implemented on existing and new equipment. Reductions in NO_x in excess of 95 percent have been demonstrated.

The purpose of this report is to update and revise the original AP-67 document by incorporating improved emissions estimates and NO_x control technology developments since 1970. Emphasis is given to identifying the significant stationary sources of NO_x emissions based on the most recent emission factors and fuel consumption data (Section 2), summarizing the developmental status of candidate NO_x control techniques (Section 3), and reviewing the effectiveness, cost and user experience with the implementation of NO_x controls on large combustion sources (Section 4), other combustion sources (Section 5), and noncombustion sources (Section 6). Also included in these sections is information on the energy and environmental impacts of the various control techniques as required by Section 108 (b)(1) of the 1977 Clean Air Act.

This report is concerned only with quantifying and controlling stationary source NO_x emissions. The effects upon health and welfare of nitrogen oxides and their secondary atmospheric reaction products are considered in two related documents, AP-63, "Air Quality Criteria for Photochemical Oxidants," and AP-84, "Air Quality Criteria for Nitrogen Oxides". Both of these documents are under revision by the Office of Air Quality Planning and Standards.

SECTION 2

CHARACTERIZATION OF NO_x EMISSIONS

This section presents a nationwide inventory and projection to the year 2000 of stationary source emissions of oxides of nitrogen. Section 2.1 defines NO_x and summarizes the basis of its occurrence in stationary source combustion. Section 2.2 describes the standard EPA method for analysis of source and ambient NO_x concentrations. Specific stationary source equipment types are described in Section 2.3. The NO_x emission factors, fuel consumption rates and annual NO_x emissions for each of these source types are also tabulated in Section 2.3. A summary of nationwide NO_x emissions and fuel consumption by equipment application sector is given in Section 2.4. Projections of these emissions to the year 2000 are given in Section 2.5.

2.1 DEFINITIONS AND FORMATION THEORY

Seven oxides of nitrogen are known to occur: NO, NO_2, NO_3, N_2O, N_2O_3, N_2O_4 and N_2O_5. Of these, nitric oxide (NO) and nitrogen dioxide (NO_2) are emitted in sufficient quantities in fuel combustion and chemical manufacturing to be significant in atmospheric pollution. In this document, "NO_x" refers to either or both of these two gaseous oxides of nitrogen. Nitrogen dioxide is deleterious to human respiratory functions and is a key participant in the formation of photochemical smog. Nitric oxide, taken alone, is relatively less harmful but is important as the main precursor to NO_2 formation in the atmosphere.

Approximately 95 percent of oxides of nitrogen emanating from stationary combustion sources are emitted as nitric oxide. Two separate mechanisms, thermal NO_x formation and fuel NO_x formation, have been identified as generating NO_x during fossil fuel combustion.

Thermal NO_x results from the thermal fixation of molecular nitrogen and oxygen in the combustion air. Its rate of formation is extremely sensitive to local flame temperature and somewhat less so to local concentration of oxygen. Virtually all thermal NO_x is formed at the region of the flame which is at the highest temperature. The NO_x concentration is subsequently "frozen" at the level prevailing in the high temperature region by the thermal quenching of the combustion gases. The flue gas NO_x concentrations are therefore between the equilibrium level characteristic of the peak flame temperature and the equilibrium level at the flue gas temperature. This kinetically controlled behavior means that thermal NO_x emissions are dominated by local combustion conditions.

Fuel NO_x derives from the oxidation of organically bound nitrogen in certain fuels such as coal and heavy oil. Its formation rate is strongly affected by the rate of mixing of the fuel and airstream in general and by local oxygen concentration in particular. The flue gas NO_x concentration due to fuel nitrogen is typically only a fraction (e.g., 20 to 60 percent) of the level which would result from complete oxidation of all nitrogen in the fuel. Thus, fuel NO_x formation, like thermal NO_x formation, is dominated by the local combustion conditions. Additionally, fuel NO_x emissions are dependent on the nitrogen content of the fuel. The NO_x emissions characterization detailed in this section, therefore, takes account of variations in equipment operating conditions and in fuel type which influences the emissions as well as the potential for control. Additional discussion on thermal and fuel NO_x formation mechanisms is given in Section 3.1.

Oxides of nitrogen emitted in the byproduct streams of chemical manufacturing (nitric acid, explosives) are predominantly in the form of NO_2. The NO_2 concentration in the flue gas is typically at the equilibrium level characteristic of the chemical compositions and temperatures required in the manufacturing process. The NO_x emissions from noncombustion sources are then much less sensitive to minor process modifications than are combustion generated NO_x emissions.

2.2 SAMPLING AND ANALYSIS METHODS

The standard EPA method for compliance testing of NO_x from stationary sources is the phenoldisulfonic acid (PDS) method. This method was developed for the measurement of nitrate in solution by Chamot around 1910 (Reference 2-1). The specifications for the PDS method are given in Reference 2-2. Briefly, the method requires that a grab sample be collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide solution which absorbs the nitrogen oxides, except nitrous oxide (N_2O). The sample is then processed following the procedures of Reference 2-2. The absorbance of 420 nm wavelength light by the treated samples is then measured. A calibrated relationship between absorbance and NO_2 concentration is used to relate the measurement to the sample NO_2 concentration.

The advantages of the PDS method include the wide concentration range, minimum number of sample handling steps, and lack of interference with sulfur dioxide in the flue gases. The disadvantages are the long time elapsed between samples, a possible interference from halides, and the inherent problems with grab sampling.

Chemiluminescence, the Federal Reference Method (Reference 2-3) for ambient NO_x sampling, is also a popular source testing technique. Although it cannot be used for compliance testing, its continuous electronic measurement feature is advantageous for use in emission control development programs.

2.3 EQUIPMENT DESCRIPTIONS, EMISSIONS ESTIMATES, EMISSION FACTORS, AND FUEL USAGE BY APPLICATION SECTOR

The rate of emission of oxides of nitrogen from stationary combustion sources is dominated by equipment design characteristics (combustion intensity, fuel/air mixing pattern, combustion gas temperature history) and fuel characteristics (combustion temperature, fuel nitrogen content). A previous NO_x emissions inventory for 1972 (Reference 2-4) classified stationary combustion sources according to the design characteristics known to influence NO_x emissions. A total of 137 combinations of equipment type and fuel type were identified as having significantly different potential for NO_x emissions and/or NO_x control. The emissions data cited in this section are an update, to 1974, of the 1972 inventory of Reference 2-4.

An overview of stationary sources of NO_x emissions is provided in Figure 2-1. The first division is by application and the second by use sector. The six applications encompass all major sources and the cited sectors include all those of importance within each sector. Steam generation is by far the largest application on a capacity basis for both utility and industrial equipment while space heating is the largest application by number of installations. Internal combustion engines (both reciprocating and gas turbines) in the petroleum and related products industries have generally been limited to pipeline pumping and gas compressor applications. Process heating data are not as readily available, but the main sources appear to be process heaters in petroleum refineries, the metallurgical industry and the drying and curing ovens in the broad-ranging ceramics industry. Incineration by both the municipal and industrial sectors is a small but noticeable source, primarily in urban areas. Noncombustion sources are largely within the area of chemical manufacture, more specifically nitric and adipic acids and explosives. The final description level in Figure 2-1 is the important equipment types. Although these equipment categories do not include all the possible variations or hybrid units, the bulk of the equipment is included in the breakdown.

The emissions inventory from Reference 2-4 for the significant stationary source equipment types was updated to 1974 using the most recent emission factors and fuel consumption data. These emission factors were obtained from EPA publication AP-42 (Reference 2-5), its three supplements (References 2-6, 2-7, 2-8) and recent field test studies (References 2-9 to 2-13). A rating of the quality and general applicability of these emission factors for each sector is given in Table 2-1.

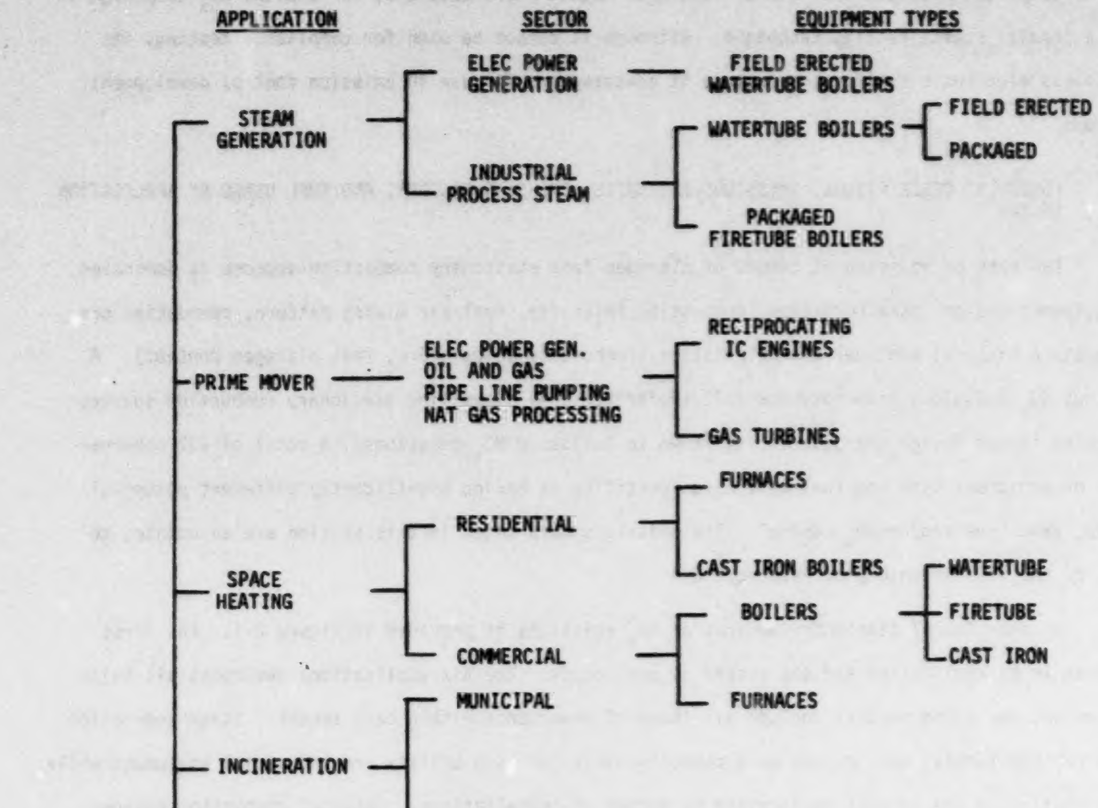

APPLICATION
SECTOR
EQUIPMENT TYPES
STATIONARY SOURCES OF NO$_X$
STEAM GENERATION
ELEC POWER GENERATION
FIELD ERECTED WATERTUBE BOILERS
INDUSTRIAL PROCESS STEAM
WATERTUBE BOILERS
FIELD ERECTED
PACKAGED
PACKAGED FIRETUBE BOILERS
PRIME MOVER
ELEC POWER GEN.
OIL AND GAS PIPE LINE PUMPING
NAT GAS PROCESSING
RECIPROCATING IC ENGINES
GAS TURBINES
SPACE HEATING
RESIDENTIAL
FURNACES
CAST IRON BOILERS
COMMERCIAL
BOILERS
WATERTUBE
FIRETUBE
CAST IRON
FURNACES
INCINERATION
MUNICIPAL
INDUSTRIAL
PROCESS HEATING
PETROLEUM REFINING
PROCESS HEATERS
FLUID CATALYTIC CRACKERS
METALLURGICAL
HEATING AND ANNEALING OVENS
COKE OVEN UNDERFIRE
OPEN HEARTH FURNACE
SINTERING OVENS
CERAMICS INDUSTRY
GLASS
BRICKS
CEMENT
KILNS
FURNACES
NONCOMBUSTION
CHEMICAL MANUFACTURING
NITRIC ACID
ADIPIC ACID
EXPLOSIVES

Figure 2-1. Stationary sources of NO$_x$ emissions.

TABLE 2-1. QUALITY OF EMISSION FACTORS FOR OXIDES OF NITROGEN.

Sector	Fuel	Quality[a]
Utility	Bituminous	A
	Lignite	B
	Anthracite	B
	Oil	A
	Gas	A
Industrial	Coal	B
	Oil	B
	Gas	B
Reciprocating IC Engines	Gas	B
	Oil	B
Gas turbines	Gas	A
	Oil	A
Residential	Gas	A
	Oil	A
Commercial	Coal	B
	Gas	A
	Oil	A
Incineration		C
Process heating		D
Noncombustion		C

[a] A — good, based on high quality field measurements
B — average, based on limited number of field measurements
C — marginal, sparse data base
D — inadequate data base

A grading of "A" means the quality of the emission factor is good, i.e., based on high quality field measurements of a large number of sources. "B" indicates average quality or based on a limited number of field measurements. "C" refers to a sparse data base, or to data which is of marginal quality and "D" indicates an inadequate data base.

The emission factors cited herein are for the baseline operating conditions without the use of NO_x controls. "Baseline" refers to nominal settings of process variables such as unit load, excess air levels, and combustion air preheat as well as to the most representative design type within a given equipment class. It should be noted that stationary source NO_x emissions are strongly dependent on small variations in design types, fuel composition or process operating conditions. Thus, for those equipment sectors given a rating other than "A" in Table 2-1, the sparseness of the available emission data may preclude the specification of a true baseline emission factor for all significant design types.

2.3.1 Utility Boilers

Emissions and Fuel Use

Utility boilers are field-erected watertube boilers ranging in thermal capacity from 30 MW (100×10^6 Btu/hr) to around 300 MW. This equipment category includes the large majority of utility and industrial electric power generating boilers. Field-erected watertube boilers operate at steam temperatures up to 840K (1050 F) and steam pressures up to 26 MPa (3800 psi). Depending upon manufacturer, units greater than about 2250 MW operate at supercritical steam pressures above 24 MPa (3500 psi) (Reference 2-14). In general, utility boilers recover up to 90 percent of the heat with waterwalled combustion chambers in combination with superheaters, reheaters, economizers and air preheaters. Approximately half of this heat energy is absorbed by radiant heat transfer to the furnace walls.

Although there are some differences among utility boiler designs in such factors as furnace volume, operating pressure, and configuration of internal heat transfer surface, the principle distinction is firing mode. This includes the type of firing equipment, the fuel handling system, and the placement of the burners on the furnace walls. The major firing modes are: single- or opposed-wall fired, tangentially fired, turbo fired, and cyclone fired. Vertically fired units and stoker units are used to a small extent in older steam generating stations. All of the major firing types can be designed to burn the principle fossil fuels — gas, oil and coal — either singly or in combination. However, the cyclone unit is primarily designed to fire coal as the principal fuel.

In addition to differences in firing mode, coal, depending on its ash characteristics, is burned in either a dry-bottom or wet-bottom (slag tap) furnace. Dry-bottom units operate at temperatures below the ash-fusion temperature, and ash is removed as a solid. Wet-bottom furnaces melt the ash and remove slag through a bottom tap. Although wet bottom units were once used extensively in burning low ash-fusion temperature coals, they are no longer manufactured due to operational problems with low sulfur coals and because their high combustion temperatures promote NO_x formation.

In single-wall firing (front-wall firing) burners are mounted normal to a single furnace wall. Furnace wall area generally limits the capacity of these units to about 1200 MW. When greater capacity is required, horizontally opposed wall-firing furnaces are normally used. In these units burners are mounted on opposite furnace walls. Generally, capacities for these units exceed 1200 MW (Reference 2-14). Burners on the single-wall and opposed-wall firing designs are usually register type where fuel and combustion air are combined in the burner throat.

Turbo-fired units are similar to the horizontally opposed-wall-fired units except that burners are mounted on opposed, downward inclined furnace walls. Fuel and combustion air are introduced into the combustion zone where rapid mixing occurs.

In tangential firing, arrays of fuel and air nozzles are located at each of the four corners of the combustion chamber. Each nozzle is directed tangentially to a small firing circle in the center of the chamber. The resulting spin of the four "flames" creates high turbulence and thorough mixing of fuel and air in the combustion zone.

In the cyclone furnace design fuel and air are introduced circumferentially into a water-cooled, cylindrical combustion chamber to produce a highly swirling, high temperature flame. The cyclone was originally developed as a slagging furnace to burn low ash-fusion temperature coals, but has recently been used successfully on lignite. Relatively high levels of thermal NO_x formation accompany the high temperatures of slagging operation. Due to the inability of this design to readily adapt to low NO_x opeartion, this type of furnace is no longer being constructed.

Vertical-firing furnaces were developed for pulverized fuels prior to the advent of water-walled combustion chambers. These units provide a long-residence time combustion which efficiently burns low-volatile fuels such as anthracite. Vertical-fired boilers are no longer sold, and relatively few of these units are found in the field.

Stoker-fired units are designed for solid fuel firing. Unlike liquid, gaseous or pulverized fuels which are burned in suspension, the stoker employs a fuel bed. This bed is either a stationary grate through which ash falls or a moving grate which dumps the ash into a hopper. The main types of stokers are overfeed and underfeed designs. Spreader stokers are overfeed designs and distribute fuel by projecting the fuel evenly over the fuel bed. Other overfeed stokers generally deposit fuel on a continuously moving grate. Underfeed designs introduce fuel beneath the fuel bed as ash is pushed aside by the newly introduced fuel.

Tangential firing, single-wall and horizontally opposed-wall firing and turbofurnace firing account for 40 and 36 and 14 percent of the fuel consumed by utility boilers (Reference 2-15). In terms of units, their distribution is 19, 59 and 8 percent, respectively. Cyclone, vertical and stoker designs make up the remaining 14 percent.

Recent trends indicate a continued strong movement toward pulverized coal-fired boilers. Many previously ordered oil-fired units are being converted to coal firing during the design phase. The trend of the last 10 years to increasing capacities appears to have slowed with many utilities electing to install two small boilers rather than a single larger unit (Reference 2-14). Industry sales were particularly depressed in 1976 and 1977. Uncertainty about the nation's energy policy, environmental regulations, mild summer load peaks, increased energy costs, and a 1975 reserve capacity of about 35 percent have combined to produce this situation.

Estimates for the uncontrolled NO_x emissions from utility boilers were derived from the 1974 utility fuel consumption compilation for coal, oil and natural gas published by the Federal Power Commission (FPC) in Reference 2-16. The consumption rate of each fuel type was prorated according to firing type based on the procedures used in Reference 2-4. Emission factors for each equipment type were obtained from AP-42 (Reference 2-5), AP-42 Supplement No. 5 (Reference 2-7), and a field test survey of utility boilers (Reference 2-10). These factors were applied to the individual fuel consumption rates to arrive at the annual NO_x figures presented in Table 2-2. The nominal heating values of the fuels were as follows: gas — 37.3 MJ/Nm^3* (1000 Btu/scf), oil — 39 GJ/m^3 (140,000 Btu/gal), and coal — 27.9 MJ/kg (12,000 Btu/lb).

A summary of the emissions and fuel usage with respect to firing type is presented in Table 2-3. The resultant total nationwide annual NO_x emissions by utility boilers in 1974 is estimated to be 5.1 Tg (5.63 million tons). The corresponding total annual fuel consumption for 1974 is 16.3 EJ (15.4 quadrillion Btu).

Fuel consumption data from References 2-4, 2-15, 2-17, and 2-18, and the present report are compared in Table 2-4. The corresponding NO_x emissions are compared in Table 2-5. The NO_x emissions for both oil and gas firing compare very well between the present report and the recent study of Reference 2-15. The discrepancy in emissions with coal firing is primarily due to the use of more recent emission factors for lignite combustion and for cyclones in this report.

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* The symbol Nm^3 is used to denote cubic meters at standard temperature and pressure.

TABLE 2-2. EMISSIONS, EMISSION FACTORS, AND FUEL USAGE FOR STEAM GENERATION, 1974 — UTILITY BOILERS[a]

Equipment Type	Firing Type	Fuel	Fuel Type	Fuel Usage PJ	Emission Factors[b] ng NO_2/J	Total NO_x Emissions[b] Gg NO_2
Field-Erected Watertube Boilers	Tangential Firing	Coal	Bituminous	4368.40	275.20	1202
			Lignite	44.01	275.20	12
		Oil	Distillate	47.72	153.51	7
			Residual	1146.33	153.51	176
		Gas	-	915.27	129.00	118
	Horizontally Opposed-Wall Firing	Coal, Dry Bottom	Bituminous	1296.83	322.50	418
			Lignite	12.63	378.40	5
		Coal, Wet Bottom	Bituminous	578.20	537.50	311
			Lignite	17.01	378.40	6
		Oil	Distillate	34.90	322.50	11
			Residual	835.98	322.50	269
		Gas	-	1454.03	301.00	437
	Front-Wall Firing	Coal, Dry Bottom	Bituminous	1296.83	322.50	418
			Lignite	12.63	378.40	5
		Coal, Wet Bottom	Bituminous	569.94	537.50	307
			Lignite	15.11	378.40	5
		Oil	Distillate	34.90	322.50	11
			Residual	835.98	322.50	269
		Gas	-	1006.70	301.00	303
	Vertical Firing	Coal, Dry Bottom	Anthracite	31.50	322.50	10
			Bituminous	399.67	322.50	129
			Lignite	3.15	322.50	1
	Cyclone	Coat, Wet Bottom	Bituminous	1076.75	559.00	601
			Lignite	13.34	378.40	5
		Oil	Distillate	3.08	322.50	1
			Residual	58.58	322.50	19
Field-Erected Watertube Boiler Stoker	Spreader	Coal	-	139.24	245.10	34
	Underfeed	Coal	-	59.71	245.10	15

[a] This table is included in Appendix A in English units.

[b] By convention NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

TABLE 2-3. ANNUAL NO_x EMISSIONS AND FUEL CONSUMPTION COMPARISON FOR UTILITY BOILERS, 1974[a]

	NO_x Emission, Tg[b] (column percent)				Fuel consumption, EJ[b] (column percent)			
Firing Type	Gas	Oil	Coal	Total	Gas	Oil	Coal	Total
Tangential	0.118 (13.8)	0.183 (24.0)	1.214 (34.8)	1.515 (29.7)	0.916 (27.1)	1.194 (39.8)	4.412 (44.4)	6.522 (40.0)
Horizontal front-wall	0.303 (35.3)	0.280 (36.7)	0.735 (21.2)	1.318 (25.8)	1.006 (29.8)	0.871 (29.05)	1.895 (19.1)	3.772 (23.1)
Opposed-wall	0.437 (50.9)	0.280 (36.7)	0.740 (21.2)	1.457 (28.5)	1.454 (43.1)	0.871 (29.05)	1.905 (19.1)	4.230 (25.9)
Cyclone		0.020 (2.6)	0.606 (17.4)	0.626 (12.3)	-	0.062 (2.1)	1.090 (11.0)	1.152 (7.1)
Vertical			0.140 (4.0)	0.140 (2.7)	-	-	0.434 (4.4)	0.434 (2.7)
Stokers			0.049 (1.4)	0.049 (1.0)	-	-	0.199 (2.0)	0.199 (1.2)
Total	0.858 (100)	0.763 (100)	3.484 (100)	5.105 (100)	3.376 (100)	2.998 (100)	9.935 (100)	16.309 (100)

[a] This table is included in Appendix A in English units.

[b] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

TABLE 2-4. ANNUAL FUEL USAGE FOR UTILITY BOILERS (EJ)[a]

Fuel	Source					
	Battelle 1971 (Reference 2-18)	MSST 1972 (Reference 2-4)	GCA 1974 (Reference 2-15)	Current 1974	Aerospace 1975, projected (Reference 2-17)	NEDS 1976[b]
Coal	5.812	8.887	8.970	9.935	9.856	10.939
Oil	2.325	2.736	3.206	2.998	2.689	3.867
Gas	4.019	3.972	3.436	3.376	3.158	4.692
Total	12.156	15.595	15.612	16.309	15.703	19.498

[a] This table is included in Appendix A in English units.

[b] Output of National Emissions Data System by Source Classification Code on August 16, 1976; contains data for 1974 and 1975.

TABLE 2-5. ANNUAL NO_x EMISSIONS FOR UTILITY BOILERS (Tg^a)[b]

Fuel	Source					
	Battelle 1971 (Reference 2-18)	MSST 1972 (Reference 2-4)	GCA 1974 (Reference 2-15)	Current 1974	Aerospace 1975, projected (Reference 2-17)	NEDS 1976[c]
Coal	2.008	3.436	4.263	3.484	4.442	4.13
Oil	0.701	0.697	0.735	0.763	0.605	1.17
Gas	1.038	1.010	0.871	0.858	0.610	0.95
Total	3.747	5.143	5.869	5.105	5.657	6.25

[a] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

[b] This table is included in Appendix A in English units.

[c] Output of National Emissions Data System by Source Classification Code on August 16, 1976; contains data from 1974 and 1975.

2.3.2 Industrial Boilers

Equipment Description

This equipment category is comprised of industrial boilers ranging in capacity up to 73.2 MW (250×10^6 Btu/hr). Industrial boilers are either field-erected or packaged units. The field-erected units are only the very large capacity units and are quite similar in design to utility boilers (See Section 2.3.1). Packaged boilers, which are equipped and shipped complete with fuel burning equipment, are mainly watertube and firetube designs. Other designs such as cast iron, and shell type are also used. Each of these designs has a fairly distinct capacity range. Packaged boilers far outnumber field-erected units, but their combined fuel consumption is slightly less than that of field-erected boilers.

In watertube boilers, hot gases pass over tubes which are water or steam filled. The tubes line the combustion chamber walls and gain heat mainly by radiative heat transfer from the flame. Downstream the combustion chamber heat is absorbed convectively with tubes mounted across the hot gas flow. Almost all package boilers greater than about 8.8 MW (30×10^6 Btu/hr) are watertube boilers.

Sales statistics for 1975 (Reference 2-19) indicate that 86 percent of the packaged watertubes were burner-fired (usually a single burner) and the remainder were stoker-fired. Of the burner-fired units, 50 percent fired either residual or distillate fuel oil, 40 percent have dual fuel (oil — natural gas) capability and 10 percent fire only natural gas. In general, natural gas and distillate oil firing units are more prevalent at the lower capacity ranges of watertube boilers.

In firetube boilers hot gases are directed from the combustion chamber through tubes which are submerged in water. Firetube boilers burn fuel oil and natural gas because the design is particularly sensitive to fouling with ash-containing fuels. Residual oil and natural gas are the most common fuels in the larger firetubes and natural gas and distillate oil are the main fuels for the smaller units. Firing is by single burner. Recent sales statistics indicate that the firetube has diminished in sales in the past 5 years (Reference 2-20).

Emission and Fuel Use

The 1974 NO_x emissions from industrial boilers were estimated by essentially the same procedure as used for utility boilers. The fuel consumption data for the total industrial boiler sector were obtained from Reference 2-18. These 1971 data were updated to 1974 by an annual growth rate estimate from Reference 2-21. The process gas consumption data were also obtained from Reference 2-18.

The fuel usage for each specific equipment type was derived from the total fuel consumption data based on the procedures used in Reference 2-4. The following were the basic assumptions made in that report in formulating the emission estimates:

- Field-erected watertube boilers larger than 29 MW (100 x 10^6 Btu/hr) are indistinguishable from utility boilers and have the same firing distribution
- Field erected watertube boilers smaller than 29 MW (100 x 10^6 Btu/hr) are single-wall-fired units
- Packaged watertube boilers are single-wall-fired units
- Packaged firetube boilers do not fire pulverized coal in significant quantities
- Alternate fuel usage (e.g., coal-derived gas) is negligible

The emission factors were largely derived from a recent field test survey of industrial boilers, Reference 2-9. The test data were screened for application to a nominal baseline operating condition. Where baseline data were available for more than one unit of a specific design type, the data were averaged. When test data for a specific firing type/fuel were unavailable, emission factors were estimated based on data for similar units. The updated emission factors based on this recent data are generally 15 to 30 percent lower for gas and oil-fired industrial boilers than those based on earlier data (Reference 2-5). The resultant estimated 1974 NO_x emissions from industrial boilers are presented in Table 2-6.

Comparisons of fuel consumption data and NO_x emission estimates from recent emission inventories for the industrial boiler sector are given in Tables 2-7 and 2-8, respectively. There are substantial differences in the fuel consumption data used in the previous inventories which cause wide discrepancies in NO_x emission estimates. These could be due to the difficulty encountered in separating the total fuel usage in the industrial sector into industrial boilers, direct heat, feed stock, internal combustion and other categories. The data used for the current estimates are regarded as the most extensive and reliable to date.

2.3.3 Commercial and Residential Space Heating

Equipment Description

This category is made up of commercial and residential warm air furnaces and boilers. Warm air furnaces are space heaters, where the unit is located in the room which it heats, or central heaters which use ducts to transport and discharge warm air into the heated space. Space heaters comprise less than 10 percent of the nation's heaters. Central heaters make up the remainder of the

TABLE 2-6. EMISSIONS, EMISSION FACTORS, AND FUEL USAGE FOR STEAM GENERATION, 1974 — INDUSTRIAL BOILERS[a]

Equipment Type	Firing Type	Fuel	Fuel Type	Fuel Usage PJ	Emission Factors[b] ng NO_2/J	Total NO_x Emissions[b] Gg NO_2
Field-Erected Watertube Boilers >29 MW	Tangential Firing	Coal	-	149.09	275.2	41
		Oil	Residual	451.08	153.5	69
		Gas	Natural	413.0	129.4	54
			Process	58.01	98.9	5
	Horizontally Opposed-Wall Firing	Coal, Dry Bottom	-	44.73	322.5	15
		Coal, Wet Bottom	-	8.95	537.5	5
		Oil	Residual	437.48	246.4	108
		Gas	Natural	488.05	129.4	63
			Process	130.55	98.9	13
	Front-Wall Firing	Coal, Dry Bottom	-	44.73	322.5	15
		Coal, Wet Bottom	-	8.95	537.5	5
		Oil	Residual	437.48	246.4	108
		Gas	Natural	330.89	129.4	43
			Process	101.20	98.9	10
	Vertical Firing	Coal, Dry Bottom	-	9.87	322.5	4
	Cyclone	Coal, Wet Bottom	-	65.23	713.8	46
		Oil	Residual	37.15	246.4	9
Field-Erected Watertube Boilers 2.9 - 29 MW	Wall Firing	Oil	Distillate	61.83	64.5	4
			Residual	308.87	184.5	57
		Gas	Natural	850.76	98.9	84
			Process	39.18	98.9	4
Field-Erected Watertube Boilers Stokers	Spreader	Coal	-	811.08	179.3	145
	Underfeed	Coal	-	459.22	179.3	83
	Overfeed	Coal	-	220.66	268.8	59
	General, Not Classified	Coal	-	107.35	179.31	19

[a] This table is included in Appendix A in English units.

[b] By convention NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

TABLE 2-6. EMISSIONS, EMISSION FACTORS, AND FUEL USAGE FOR STEAM GENERATION, 1974 — INDUSTRIAL BOILERS (Concluded)[a]

Equipment Type	Firing Type	Fuel	Fuel Type	Fuel Usage PJ	Emission Factors[b] ng NO_2/J	Total NO_x Emissions[b] Gg NO_2
Packaged Watertube		Coal	-	44.73	322.0	15
	Wall Firing	Oil	Distillate	154.88	67.5	11
			Residual	831.80	184.5	153
		Gas	Natural	2675.22	98.9	265
			Process	139.71	98.9	14
Packaged Watertube Stoker	Spreader	Coal	-	383.93	179.3	69
	Underfeed	Coal	-	598.82	179.3	107
	Overfeed	Coal	-	95.42	268.8	25
	General, Not Classified	Coal	-	62.62	179.3	11
Packaged Firetube Scotch	Wall Firing	Oil	Distillate	154.88	67.5	11
			Residual	775.58	184.5	143
		Gas	Natural	846.74	98.9	83
			Process	20.0	98.9	2
Packaged Firetube Firebox	Wall Firing	Oil	Distillate	59.55	67.5	4
			Residual	306.29	184.5	56
		Gas	Natural	731.36	98.9	73
			Process	20.0	98.9	2
Packaged Firetube Firebox Stoker	Spreader	Coal	-	17.89	179.3	4
	Underfeed	Coal	-	89.46	179.3	16
	Overfeed	Coal	-	11.93	268.8	4
Packaged Firetube HRT	Wall Firing	Oil	Distillate	29.78	67.51	2
			Residual	161.19	184.5	30
		Gas	-	384.89	98.9	38
Packaged Firetube HRT Stoker	Spreader	Coal	-	8.95	179.3	2
	Underfeed	Coal	-	44.73	179.3	8
	Overfeed	Coal	-	5.96	268.8	2

[a] This table is included in Appendix A in English units.

[b] By convention NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x stationary source combustion is emitted as NO.

TABLE 2-7. ANNUAL FUEL CONSUMPTION FOR INDUSTRIAL BOILERS (EJ)[a]

Fuel	Source					
	Battelle 1971 (Reference 2-18)	MSST 1972 (Reference 2-4)	GCA 1973 (Reference 2-15)	Current 1974	Aerospace 1975, projected (Reference 2-17)	NEDS, 1976[b]
Coal	2.962	1.865	1.445	3.294	1.450	2.014
Oil	3.784	5.844	1.794	4.208	2.839	3.871
Gas	6.044	4.412	5.486	6.721	3.714	27.689
Process Gas	0.509	0.322	-	0.509	1.836	c
Total	13.299	12.443	8.725	14.732	9.830	33.574

[a] This table is included in Appendix A in English units.

[b] Output of National Emissions Data System on August 16, 1976; contains data from 1974 and 1975.

[c] 9.91×10^{10} m^3 of process gas of unspecified heat content.

TABLE 2-8. ANNUAL NO_X EMISSIONS FROM INDUSTRIAL BOILERS (Gg^a)[b]

Fuel	Source					
	Battelle 1971 (Reference 2-16)	MSST 1972 (Reference 2-4)	GCA 1973 (Reference 2-14)	Current 1974	Aerospace 1975, projected (Reference 2-15)	NEDS 1976[c]
Coal	806	467	535	700	537	658
Oil	659	996	390	765	416	405
Gas	493	449	381	753	275	715[d]
Total	1968	1912	1316	2218	1228	1778

[a] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

[b] This table is included in Appendix A in English units.

[c] Output of National Emissions Data System on August 16, 1976; contains data from 1974 and 1975.

[d] Includes 87Gg due to process gas.

warm air heater equipment sector. Combustion chambers are cylindrical for distillate oil firing or sectional for natural gas firing. Combustion products pass through flue gas passages of the heat exchanger and exit through a flue to the atmosphere. The commercial packaged boilers are very similar to industrial packaged boilers (See Section 2.3.2). Boilers used for residential space heating are generally cast iron designs. Residential warm air furnaces and cast iron boilers are available in sizes up to 0.12 MW (4 x 10^5 Btu/hr). Larger units are mainly confined to the commercial and institutional sector.

Commercial and institutional systems are used for space heating and hot water generation. The equipment consists mainly of oil-fired warm air furnaces and firetube boilers. The rated heat input, or fuel consumption, of this equipment ranges from 0.12 MW (4 x 10^5 Btu/hr) to 3.6 MW (12.5 x 10^6 Btu/hr).

Fuels burned for residential and commercial space heating are residual and distillate oil, natural gas and occasionally coal. Typically residual oil firing is limited to the larger commercial or institutional boilers.

Although there has been a continuing trend in the recent past toward space heating equipment which uses natural gas, this trend is expected to reverse itself in the near future (Reference 2-22). Furthermore, the use of fossil fuels of all types is expected to drop drastically by the year 2000.

Emissions and Fuel Use

The fuel consumption data for commercial and residential space heating equipment were obtained from the National Gas Survey (Reference 2-23). The fuel consumption data were subdivided by equipment type based on the procedures of Reference 2-4. The basic assumptions made in that study were:

- Coal is burned in commercial units (stokers) but not in residential systems
- No pulverized coal is burned in commercial or residential units
- Residual oil consumption is negligible in residential units
- Commercial fuel usage is directly proportional to installed capacity
- LPG, wood, or producer gas have negligible use in space heating

The emission factors used were obtained from AP-42 (Reference 2-5), AP-42 Supplement No. 6 (Reference 2-8), and Reference 2-24.

The NO_x emissions estimates by equipment type for the commercial and residential sector are presented in Tables 2-9 and 2-10, respectively. A summary of these results by sector is given is Table 2-11.

TABLE 2-9. EMISSIONS, EMISSION FACTORS, AND FUEL USAGE FOR COMMERCIAL BOILERS, 1974[a]

Equipment Type	Firing Type	Fuel	Fuel Type	Fuel Usage PJ	Emission Factors[b] ng NO_2/J	Total NO_x Emissions[b] Gg NO_2
Packaged Firetube Scotch	Wall Firing	Oil	Distillate	545.07	67.5	36.8
			Residual	545.07	184.9	100.8
		Gas	-	691.46	98.9	68.0
Packaged Firetube Firebox	Wall Firing	Oil	Distillate	545.07	67.5	36.8
			Residual	545.07	184.0	100.8
		Gas	-	691.46	98.9	68.0
Packaged Firetube Firebox, Stoker	All Categories	Coal	-	174.83	179.3	31.7
Packaged Firetube HRT	Wall Firing	Oil	Distillate	272.54	67.5	18.4
			Residual	272.54	184.9	50.3
		Gas	-	345.73	98.9	34.5
Packaged Firetube HRT, Stoker	All Categories	Coal	-	87.42	179.3	15.4
Packaged Firetube, General, Not Classified	Wall Firing	Oil	Distillate	91.69	67.5	6.2
			Residual	84.31	184.9	15.6
		Gas	-	115.25	44.3	5.1
	Stoker and Handfire	Coal	-	19.42	107.5	2.1
Packaged Cast Iron Boilers	Wall Firing	Oil	Distillate	272.54	67.5	18.4
			Residual	272.54	184.9	50.3
		Gas	-	432.16	51.6	22.7
Packaged Watertube Coil	Wall Firing	Oil	Distillate	29.55	67.5	2.0
			Residual	36.17	184.9	6.7
		Gas	-	46.09	44.3	2.1
Packaged Watertube Firebox	Wall Firing	Oil	Distillate	17.78	67.5	1.2
			Residual	24.10	184.9	4.4
		Gas	-	19.21	44.3	0.8
Packaged Watertube, General, Not Classified	Wall Firing	Oil	Distillate	29.55	67.5	2.0
			Residual	36.17	184.9	6.7
		Gas	-	46.09	44.3	2.1

[a] This table is included in Appendix A in English units.

[b] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

TABLE 2-10. EMISSIONS, EMISSION FACTORS, AND FUEL USAGE FOR RESIDENTIAL SPACE HEATING, 1974[a]

Equipment Type	Firing Type	Fuel	Fuel Type	Fuel Usage PJ	Emission Factors[b] ng NO_2/J	Total NO_x Emissions[b] Gg NO_2
Steam or Hot Water Heaters	Single Burner	Oil	Distillate	1273.90	55.04	70.1
		Gas	-	1055.12	35.26	37.2
Hot Air Furnaces	Single Burner	Oil	Distillate	1405.19	55.04	77.3
		Gas	-	3090.94	35.26	108.9
Floor, Wall, or Pipeless Heaters	Single Burner	Oil	Distillate	210.07	55.04	11.5
		Gas	-	712.17	35.26	25.1
Room Heater With Flue	Single Burner	Oil	Distillate	315.10	55.04	17.3
		Gas	-	738.56	35.26	26.0
Room Heater Without Flue	Single Burner	Oil	Distillate	201.28	35.26	7.1

TABLE 2-11. SUMMARY OF ANNUAL NO_x EMISSIONS AND FUEL CONSUMPTION FOR COMMERCIAL AND RESIDENTIAL SPACE HEATING, 1974[a]

Sector	NO_x Emission (Column %)[b] Gg NO_2				Fuel Consumption (Column %) EJ			
	Oil	Gas	Coal	Total	Oil	Gas	Coal	Total
Commercial	457.4 (71.4)	203.3 (50.8)	49.2 (100)	709.9 (65.1)	3.620 (51.5)	2.387 (29.9)	0.282 (100)	6.289 (41.1)
Residential	183.3 (28.6)	197.2 (49.2)	-	380.5 (34.9)	3.406 (48.5)	5.597 (70.1)	-	9.003 (58.9)
Total	640.7 (100)	400.5 (100)	49.2 (100)	1090.4	7.026 (100)	7.984 (100)	0.282 (100)	15.292 (100)

[a] This table is included in Appendix A in English units.

[b] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

Thirty percent of the total fossil fuel used in the United States in stationary sources is consumed in space heating. According to the 1970 United States Census, 57.7 percent of residential heating equipment was gas-fired, 28.3 percent was oil-fired, and the remaining 14 percent used other fuels such as propane, coal, and wood. Fuel consumption data for the combined commercial/residential sector obtained from several sources are compared in Table 2-12. The fuel usage used in this report compares very well with those from the FEA for 1974. The NO_x emission estimates by fuel are compared with several recent sources for the commercial and residential sector in Tables 2-13 and 2-14. The estimates are in reasonable agreement.

2.3.4 Internal Combustion

2.3.4.1 Stationary Reciprocating Internal Combustion Engines

Reciprocating IC engines for stationary applications range in capacity from 15 kW (20 hp) to 37 MW (50,000 hp). These engines are either compression ignition (CI) units fueled by diesel oil or a combination of natural gas and diesel oil (dual), or spark ignition (SI) fueled by natural gas or gasoline.

Stationary reciprocating IC engines use two methods to ignite the fuel-air mixture in the combustion chamber. In CI engines, air is first compression heated in the cylinder, and then diesel fuel is injected into the hot air where ignition is spontaneous. In SI engines, combustion is spark initiated with the natural gas or gasoline being introduced either by injection or premixed with the combustion air in a carburetted system. Either 2- or 4-stroke power cycle designs with various combinations of fuel charging, air charging, and chamber design are available.

Because reciprocating IC engine installations characteristically have a low physical profile (low buildings, short stacks, and little visible emissions), they are frequently located in or adjacent to urban centers where power demands are greatest and pollution problems most acute. These units are used in a variety of applications because of their relatively short construction and installation time and the fact that they can be operated remotely. Applications range from shaft power for large electrical generators to small air compressors and welders.

By capacity, 73 percent of the IC engines are fueled by natural gas, 16 percent by diesel oil and 11 percent by gasoline. In terms of installed capacity, the oil and gas industry is the leading user of stationary IC engines for pipeline and production applications, followed by general industrial users, electric power generation, and agriculture. In terms of annual energy consumption, oil and gas industry applications again come first, followed by general industrial and electrical generation applications.

TABLE 2-12. ANNUAL FUEL USAGE FOR THE COMMERCIAL/RESIDENTIAL SECTOR, (EJ)[a]

Fuel	Source								
	AP-73 1968 (Ref. 2-25)	AP-115 1969 (Ref. 2-26)	Bureau of Mines 1970 (Ref. 2-27)	MSST 1972 (Ref. 2-4)	FEA 1973 (Ref. 2-28)	GCA 1973 (Ref. 2-15)	Current 1974	FEA 1974 (Ref. 2-28)	FEA 1975 (Ref. 2-28)
Coal	0.580	0.428	0.430	0.245	0.311	0.367	0.282	0.313	0.219
Oil	4.380	4.412	6.794	6.288	7.466	4.915	7.026	7.056	6.689
Gas	6.884	7.366	7.771	8.082	7.994	7.769	7.984	7.836	8.049

[a] This table is included in Appendix A in English units.

TABLE 2-13. ANNUAL NO_x EMISSIONS FROM COMMERCIAL BOILERS (Gg^a)[b]

Fuel	Source			
	Battelle 1971 (Reference 2-18)	MSST 1972 (Reference 2-4)	GCA 1973 (Reference 2-15)	Current 1974
Coal	119	26	27	49
Oil	134	192	570	457
Gas	23	109	100	203
Total	276	327	697	709

[a] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

[b] This table is included in Appendix A in English units.

TABLE 2-14. ANNUAL NO_x EMISSIONS FROM RESIDENTIAL SPACE HEATING (Gg^a)[b]

Fuel	Source			
	Battelle 1971 (Reference 2-18)	MSST 1972 (Reference 2-4)	GCA 1973 (Reference 2-15)	Current 1974
Coal	-	-	11	-
Oil	153	230	89	183
Gas	162	192	190	197
Total	315	422	290	380

[a] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

[b] This table is included in Appendix A in English units.

The emissions estimates for reciprocating IC engines, given in Table 2-15, were derived from Reference 2-11. This is the most recent and complete survey of emissions from reciprocating IC engines. Since the horsepower, speed, cycle, fuel, air charging, and fuel charging combinations are so numerous, emission estimates for each combination would be impossible considering the data available. In view of this fact, the IC engine emissions are categorized into spark-ignition (gas-fired), and compression ignition (diesel or dual-fueled). The fuel data of Reference 2-11 were updated to 1974 by the FPC data from Reference 2-16.

2.3.4.2 Gas Turbines

Gas turbines are rotary internal combustion engines fueled by natural gas, diesel or distillate fuel oils, and occasionally residual or crude oils. These units range in capacity from 30 kW (40 hp) to over 74 MW (100,000 hp) and may be installed in groups for larger power output. The basic gas turbine consists of a compressor, combustion chambers, and a turbine. The compressor delivers pressurized combustion air to the combustors at compression ratios of up to 20 to 1. Injectors introduce fuel into the combustors and the mixture is burned with exit temperatures up to 1,370K (2,000F). The hot combustion gases are rapidly quenched by secondary dilution air and then expanded through the turbine which drives the compressor and provides shaft power. In some applications, exhaust gases are also expanded through a power turbine.

While simple-cycle gas turbines have only the three components described above, regenerative-cycle gas turbines also use hot exhaust gases (700K to 870K, 800F to 1,100F) to preheat the inlet air between the compressor and the combustor. This makes it possible to recover some of the thermal energy in the exhaust gases and to increase thermal efficiency. A third type of turbine is the combined-cycle gas turbine. This is basically a simple-cycle unit which exhausts to a waste heat boiler to recover thermal energy from the exhaust gases. In some cases, this waste heat boiler is also designed to burn additional fuels to supplement steam production, a process which is referred to as supplementary firing.

Gas turbines have been extremely popular in the past decade because of the relatively short construction lead times, low cost, ease and speed of installation, and low physical profile (low buildings, short stacks, little visible emissions, quiet operation). In addition, features like remote operation, low maintenance, high power-to-weight ratio, and short startup time have added to their popularity. Primary applications of gas turbines include electricity generation (peaking and baseload), pumping, gas compression, standby electricity generation, and miscellaneous industrial uses.

The fuel data for gas turbines were obtained from the Shell Report (Reference 2-29) and updated to 1974 by data from the same FPC source mentioned above. Emission factors were obtained from AP-42 Supplement No. 4 (Reference 2-6). NO_x emissions for gas turbines are shown in Table 2-15.

TABLE 2-15. EMISSIONS, EMISSION FACTORS, AND FUEL USAGE BY EQUIPMENT CATEGORY FOR INTERNAL COMBUSTION ENGINES, 1974[a]

Equipment Type	Firing Type	Fuel	Fuel Usage PJ	Emission Factors,[b] ng NO_2/J	Total NO_x Emissions[b] Gg
Reciprocating Engines	Spark ignition	Gas	1063.16	1892.0	2011
	Diesel >373 kW	Oil	67.27	1788.8	120
	Diesel <373 kW	Oil	146.96	1466.3	215
		Dual	53.82	1251.3	67
Gas Turbines		Gas	642.35	193.5	130
		Oil	301.35	365.5	110

[a] This table is included in Appendix A in English units.

[b] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

Comparisons of fuel data and NO_x emission estimates from several recent surveys are given in Tables 2-16 and 2-17, respectively. The lower emissions from gas turbines from this report, compared to those from the earlier inventory, Reference 2-4, are mainly due to the smaller and more recent emission factors obtained from AP-42 Supplement No. 4 mentioned previously.

2.3.5 Industrial Process Heating

Significant quantities of fuel are consumed by industrial process heating equipment in a wide variety of industries, including iron and steel production, glass manufacture, petroleum refining, cement manufacture, sulfuric acid manufacture, and brick and ceramics manufacture. In addition, there are dozens of industrial processes that burn smaller amounts of fuel, such as coffee roasting, drum cleaning, paint curing ovens, and smelting of metal ores, to name only a few. Brief process descriptions for some of these are given below.

Iron and Steel Industry

The iron and steel industry is one of the major contributors to combustion-related process NO_x emissions. The most important combustion processes are sinter lines, coke ovens, open hearth furnaces, soaking pits and reheat furnaces. The remaining combustion-related processes (pelletizing, heat treating, and finishing) are less important because they use relatively small amounts of fuel (Reference 2-9).

Sintering machines are used to agglomerate ore fines, flue dust, and coke breeze for charging of a blast furnace. The use of this operation is presently declining at the rate of about 3.4 percent annually because of its inability to accommodate rolling mill scale which is contaminated with rolling oil.

Coke ovens produce metallurgical coke from coal by the distillation of volatile matter producing coke oven gas. The fuels commonly used in this process are coke oven gas and blast furnace gas. Although NO_x emissions are minimized by slow mixing in combustion chambers, they are nonetheless substantial because of the very large quantity of fuel consumed in this process. Present projections show a 5.7 percent annual increase in fuel consumption for coke ovens.

Open hearth furnaces are now being replaced in the U.S. steel industry by the basic oxygen furnace, but are still an important source of NO_x emissions because of the very high combustion air preheat temperature, high operating temperatures, and the practice of oxygen lancing. Fuel consumption in open hearth furnaces is presently decreasing about 8 percent per year.

Soaking pits and reheat furnaces are used to heat steel billets and ingots to correct working temperatures prior to forming. Current trends are toward continuous casting of molten metal,

TABLE 2-16. ANNUAL FUEL CONSUMPTION BY INTERNAL COMBUSTION ENGINES (PJ)[a]

Fuel	Source		
	Shell 1971 (Reference 2-29)	MSST 1972 (Reference 2-4)	Current 1974
Oil and Dual	503	548	569
Gas	1579	1716	1706

[a] This table is included in Appendix A in English units.

TABLE 2-17. ANNUAL NO_x EMISSIONS FROM INTERNAL COMBUSTION ENGINES (Gg[a])[b]

Equipment	Fuel	Source		
		Shell 1971 (Reference 2-29)	MSST 1972 (Reference 2-4)	Current 1974
Reciprocating Engines	Oil and Dual	360	287	399
	Gas	1580	1697	2014
Turbines	Oil	30	108	109
	Gas	70	156	127
Total		2040	2248	2649

[a] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

[b] This table is included in Appendix A in English units.

and the need for these units is being eliminated. At present, however, soaking pits and reheating furnaces still consume more fuel than any other single process in the steel industry. In spite of the fact that soaking pits and reheat furnaces are being phased out, consumption of process fuel continues to increase at an annual rate of about 2.8 percent in the iron and steel industry as a whole.

Glass Industry

In the glass industry, melting furnaces and annealing lehrs are the two fuel combustion processes of greatest importance. Melters in the glass industry are continuous reverbatory furnaces fueled by natural gas and oil. Coal is not suitable for these furnaces because of its inherent impurities. Annealing lehrs control the cooling of the formed glass to prevent stains from occurring. Some lehrs are direct-fired by atmospheric, premix, or excess-air burners. About 80 percent of the total industry fuel consumption goes for melting, while annealing lehrs consume about 15 percent. There is a current trend in the glass industry towards electric melters, or at least electrically assisted conventional melters. But until it becomes clearer which fuels are going to be available in the future, no definite trends will emerge. Present trends toward fuel oil in place of natural gas have begun as a result of natural gas shortages and price increases.

Cement Industry

Cement kilns are the major combustion processes in the cement industry. These kilns are rotary cylindrical devices up to 230 m (750 feet) in length which contain a feedstock combination of calcium, silicon, aluminum, iron, and various other trace metals. This mixture of elements in the form of various combinations of clay, shale, slate, blast furnace slag, iron ore, silica sand, limestone, and chalk slowly moves through the kiln as products of fossil fuel combustion move in an opposite direction. Temperatures of the material during the process may reach 1,756K (2,700F).

Coal, fuel oil, and natural gas are the main fuels used in cement kilns. Natural gas accounts for 45 percent of the fuel consumed, coal for 40 percent, and fuel oil for 15 percent. The major effluent stream for this process is the exhaust gas which passes through the entire length of the kiln and may entrain additional particulate or trace metals from the kiln feedstock. Cement industry figures show that the industry has grown an average of about 1.9 percent annually over the past 20 years. Industry projections, however, predict a greater growth in the next few years of between 2.6 to 4.1 percent per year (Reference 2-30).

Petroleum Refineries

A wide variety of process combustion takes place in the petroleum refining industry, including catalyst regenerating in the catalytic cracker, catalytic reforming, delayed coking, and hydrotreating and flaring of waste gases. Catalytic cracking is required for a large portion of gasoline production. Fuel is consumed in this operation in the catalyst regeneration procedure which removes coke and tars from the catalyst surface. Temperatures during this process are moderate, ranging from 840 to 922K (1,050 to 1,200F), but fuel requirements are on the order of 829kJ/l (125,000 Btu/Bbl) feedstock. Catalytic cracking capacity increased about 1.7 percent per year between 1960 and 1973. Future growth will depend on energy and environmental policy and particularly the demand for low sulfur fuel oil. Present estimates of future growth are from 1 percent to 3.0 percent per year (Reference 2-30).

Catalytic reforming, where certain saturated ring hydrocarbons are converted into aromatic compounds, typically utilizes oil, gas, or electricity as its primary fuel. Delayed coking is an energy extensive process which uses severe cracking to convert residual pitch and tar to gas, naptha, heating oil and other more valuable products. Hydrotreating is a process designed to remove impurities such as sulfur, nitrogen, and metals to prepare cracking or reformer feedstock.

Process heating fuels used by the refinery industry are primarily natural gas and refining gas, along with some residual oils and petroleum coke. Projections are for a 2.7 percent annual increase in process heating to 1980, and 2.9 percent per year to 1985 (Reference 2-30). The fuel mix for the future is highly dependent on both availability and costs of the preferred fuels, and is therefore very difficult to project until national energy priorities are established and the question of natural gas price regulations is settled.

Brick and Ceramic Kilns

Brick and ceramic kilns for curing clay products are another major user of process heating fuels. Products of these kilns include structural bricks, structural and facing tile, vitrified clay pipe, and other related items. Typically a kiln is operated in conjunction with a drier which recovers part of the heat contained in the exhaust gases. Kilns are fueled by coal, oil, or gas (depending on the availability of fuel and the product being cured) for batch runs of 50 to 100 hours at temperatures around 1,367 K (2,000 F). Combustion products are ducted from the kiln to a drier, where wet clay products undergo an initial drying process. Occasionally, when higher temperatures are needed for drying, a secondary combustion process is used in the drier itself.

Emissions

Emissions from the industrial process equipment sector are regarded as the most difficult to quantify of all stationary sources. This is largely due to the extreme diversity of equipment types in use and is compounded by the common practice of reporting industrial fuel use by sector rather than by equipment type. The annual nationwide NO_x emissions estimates for the significant emitters in the industrial process heating sector are given in Table 2-18. A number of minor equipment types are excluded from this table, as insignificant on a national scale, but could be important from the standpoint of localized pollution potential. The data sources used to generate Table 2-18 include References 2-4 and 2-31 through 2-35. The nationwide emissions for the industrial process sector are estimated to be 432.2 Gg (0.476 x 10^6 tons) per year which comprises 3.5 percent of the nationwide total from all stationary sources. Table 2-18 also shows estimates for some process equipment types from a recent output from the National Emissions Data System (NEDS) and from a recent IGT study (Reference 2-36). Major discrepancies exist in the estimate for glass melting furnaces and for heating/annealing ovens. Further study should therefore be made before these data are used to evaluate the need for control measures for these sources.

2.3.6 Incineration

NO_x emissions estimates due to incineration are taken from the OAQPS survey, Reference 2-32. NO_x emissions from open or prescribed burning are not included in this category. OAQPS reported a total NO_x production due to incineration of 37 Gg (41,000 tons). The 1971 estimate was updated to 1974 using population growth and GNP data obtained from the Bureau of Census, Reference 2-35, and is presented in Table 2-19. The total NO_x emissions from incineration are thus estimated to be 39 Gg (43,000 tons) per year and may be compared to the AP-115 (Reference 2-26) estimate for 1969 of 64 Gg (70,000 tons) NO_x and the 1976 NEDS National Emissions Summary value of 42 Gg (46,000 tons) NO_x. In view of the broad spectrum covered by the industrial incineration sector, these discrepancies are not surprising.

2.3.7 Noncombustion Sources

NO_x emissions for the chemical industry dominate this category. Again, OAQPS, Reference 2-32, data are used exclusively for nitric acid production, sulfuric acid production, and explosives manufacture. The emissions for these sources were updated to 1974 by production data obtained from the Bureau of Census, Reference 2-35, and are presented in Table 2-20. Personal communication with GCA Corporation yielded emission estimates for adipic acid plants. The total NO_x emission from these noncombustion sources amounts to 203 Gg (0.224 million tons) per year. Nitric acid production

TABLE 2-18. SUMMARY OF ANNUAL EMISSIONS FOR INDUSTRIAL PROCESS HEATING EQUIPMENT (Gg[a])[b]

Industry	Application	Fuel	Current NO_x Estimates for 1974	NEDS 1976	IGT (Reference 2-31)
Glass	Melting	Oil	56.7	8.3	-
	Furnace	Gas	10.6		
Petroleum	Catalytic cracker	-	45.4	31.5	-
	Process heaters	Oil/Gas	146.9	118.8	-
Cement	Drying kilns	All	98.9	-	97.0
Steel and Iron	Coke oven overfire	Gas	5.4	18.9	26.9
	Heating annealing ovens	Oil/Gas	6.3	-	117.0
	Open hearth ovens	-	20.0	-	48.3
	Sintering	-	26.5	2.0	29.6
Bricks	Curing	Oil/Gas	7.3	-	-
Misc.	Flares	Gas	8.2	-	-

[a] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

[b] This table is included in Appendix A in English units.

TABLE 2-19. SUMMARY OF ANNUAL NO_x EMISSIONS FROM INCINERATION[a]

Industry	Application	Total NO_x Emissions[b] Gg
Incineration	Industrial	21.8
	Municipal	17.2
Total		39.0

TABLE 2-20. SUMMARY OF ANNUAL EMISSIONS FROM NONCOMBUSTION SOURCES[a]

Industry	Application	NO_x, Gg[b]
Acid	Sulfuric	10.9
	Nitric	127.0
	Adipic	14.5
Explosives		50.9
Total		203.3

TABLE 2-21. ESTIMATES OF ANNUAL NO_x EMISSIONS FROM OTHER SOURCES

Source	NO_x, Gg[b]
Solid waste disposal	150
Forest wildfires	138
Prescribed burning	30
Agriculture burning	13
Coal refuse fires	53
Structural fires	6
Misc. (welding, grain silos, etc.)	45
Total	435

[a] These tables are included in Appendix A in English units.

[b] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

is by far the largest source of noncombustion NO_x emissions, contributing nearly 62 percent of the total. Although NO_x emissions from the manufacture of sulfuric acid are a result of combustion of sulfur in the feedstock with gas or oil, this source is included here rather than with the combustion sources.

2.3.8 Other NO_x Emissions

Other sources of NO_x emissions include forest fires, prescribed burning, and structural fires. Estimates of emissions from these sources are very inconsistent. A composite of estimates and data from several sources (References 2-32, and 2-35, and the 1976 NEDS National Emission Report) is given in Table 2-21.

2.4 SUMMARY OF 1974 NO_x EMISSIONS AND FUEL CONSUMPTION

This section presents a summary of the 1974 estimated NO_x emissions and fuel consumption by sector and fuel. This will be followed by comparisons with other sector inventories, primarily References 2-4 and 2-15.

A summary of total NO_x emissions by fuel and sector compiled from the best available data is presented in Table 2-22. Table 2-23 summarizes the 1974 fuel consumption by sector. The NO_x emissions estimates are further summarized in Figure 2-2. Tables 2-24 and 2-25 compare these data with previous estimates: MSST, Reference 2-4; GCA, Reference 2-15; ESSO, Reference 2-31; AP-115, Reference 2-26; and OAPQS, Reference 2-32. Exact comparison to other sources is virtually impossible since each chose to present NO_x sources grouped under different headings. These tables demonstrate that the present set of data, while based on much more detailed breakdowns, are in reasonable agreement with previous estimates.

2.5 NO_x EMISSION TRENDS AND PROJECTIONS

Nationwide NO_x emission trends from 1940 to 1972 as compiled by the EPA (Reference 2-37) are illustrated in Figure 2-3. In general, stationary sources comprise between 60 and 70 percent of the total NO_x production, as shown in the figure. Figure 2-4 compares the EPA figures with the ESSO (Reference 2-31) estimates published in 1968. The slight downward trend in 1971 of the EPA data is due to revised emission factors. As can be seen from the figure, 1972 emissions have already attained the 1978 ESSO estimate.

Projections for nationwide NO_x emissions from stationary sources have been made by the National Academy of Sciences (Reference 2-37) based on several assumptions, including consideration for various control options. These projections with extrapolation to the year 2000 are presented in Table 2-26. Assumptions made for these projections are:

TABLE 2-22. SUMMARY OF TOTAL ANNUAL NO_x EMISSIONS FROM FUEL USER SOURCES, 1974[a]

Sector	NO_x Production Tg^b (percent of total)			Totals by Sector Tg^b (percent of total)	Cumulative Percentage
	Gas	Coal	Oil		
Utility Boilers	0.858 (7.0)	3.484 (28.6)	0.763 (6.3)	5.105 (41.9)	41.9
IC Engines					
Reciprocating	2.014 (16.5)	-	0.399 (3.3)	2.413 (19.8)	61.7
Gas Turbines	0.127 (1.1)	-	0.109 (0.9)	0.236 (2.0)	63.7
Industrial Boilers	0.753 (6.2)	0.700 (5.8)	0.765 (6.3)	2.218 (18.2)	81.9
Commercial/Residential Heating	0.400 (3.3)	0.049 (0.4)	0.641 (5.3)	1.090 (9.0)	90.9
Process Heating	-	-	-	0.432 (3.5)	94.4
Noncombustion	-	-	-	0.203 (1.7)	96.1
Incineration	-	-	-	0.039 (0.3)	96.4
Others	-	-	-	0.435 (3.6)	100.0
Total	4.152 (34.1)	4.233 (34.8)	2.677 (22.1)	12.171 (100)	

[a] This table is included in Appendix A in English units.

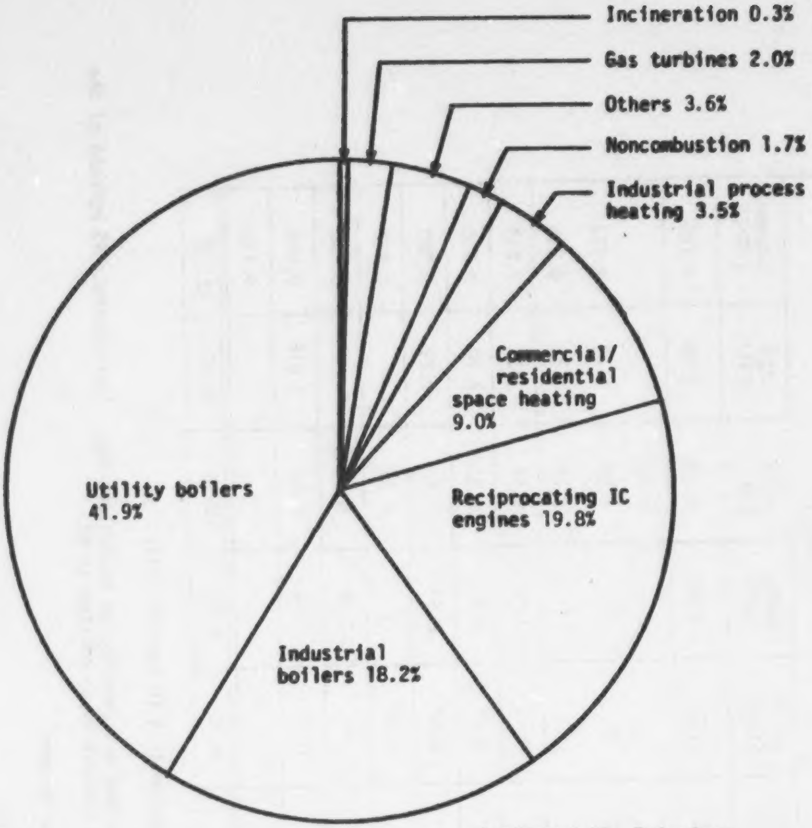
[b] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

TABLE 2-23. SUMMARY OF ANNUAL FUEL USAGE[a], 1974

Sector	Fuel Usage[b] — EJ (percentage of total)			Total
	Gas	Coal	Oil	
Utility Boilers	3.376 (6.95)	9.935 (20.44)	2.998 (6.16)	16.309 (33.55)
IC Engines				
Reciprocating	1.063 (2.19)	—	0.268 (0.55)	1.331 (2.74)
Turbines	0.642 (1.32)	—	0.301 (0.62)	0.943 (1.94)
Industrial Boilers	7.230 (14.87)	3.294 (6.78)	4.208 (8.66)	14.732 (30.31)
Commercial Boilers	2.387 (4.91)	0.282 (0.58)	3.620 (7.45)	6.289 (12.94)
Residential Heating	5.597 (11.51)	—	3.406 (7.01)	9.003 (18.52)
TOTAL	20.295 (41.75)	13.511 (27.80)	14.801 (30.45)	48.607 (100.0)

[a] This table is included in Appendix A in English units.

[b] Excludes process fuel.



Source	Estimated NO_x Emissions	
	Tg	10^6 Tons
Utility Boilers	5.105	5.628
Industrial Boilers	2.218	2.444
Reciprocating IC Engines	2.413	2.660
Commercial/Residential Heating	1.090	1.202
Industrial Process Heating	0.432	0.476
Noncombustion	0.203	0.224
Gas Turbines	0.236	0.260
Incineration	0.039	0.043
Other	0.435	0.479
TOTAL	12.171	13.416

Figure 2-2. Summary of 1974 stationary source NO_x emissions.

TABLE 2-24. COMPARISONS OF ANNUAL NO_X EMISSIONS DATA[a]

Sector	Tg (NO_2)[b]					
	ESSO (1968)	AP-115 (1970)	OAPQS (1971)	MSST (1972)	GCA (1973)	Current (1974)
Utility Boilers	3.48	4.27	4.88	5.14	5.90	5.105
IC Engines				(2.25)		
Reciprocating	1.90[d]	f	f	1.99	1.49	2.413
Gas Turbines	c	f	f	0.26	0.45	0.236
Industrial Boilers	2.55	4.11	3.54	1.91	1.31	2.218
Commercial	0.91	0.21	0.53	0.33	0.70	0.710
Residential	0.91	0.52	0.53	0.42	0.29	0.380
Process Heating	c	0.18	c	0.35	—	0.432
Noncombustion	0.22	—	0.18	0.14	—	0.203
Incineration	c	0.07	0.04	0.04	0.015	0.039
Other	e	e		e		0.435
TOTAL	9.97	9.36	9.70	10.58	10.15	12.171

[a] This table is included in Appendix A in English units.

[b] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

[c] Included in industrial size boilers.

[d] Pipeline and gas plants only.

[e] Not included in data.

[f] Included in utility and industrial depending on use.

TABLE 2-25. ANNUAL FUEL CONSUMPTION COMPARISONS[a]

Sector	EJ				
	OAPQS (1971)	AP-115 (1969)	MSST (1972)	GCA (1973)	Current (1974)
Utility Boilers	14.81	12.81	15.60	15.61	16.309
IC Engines					
Reciprocating	—	—	1.33	2.12	1.331
Gas Turbine	—	—	0.94	1.41	0.944
Industrial Boilers	17.79[b]	17.00[b]	12.44	8.72	14.732
Commerical	12.87	12.21	4.36	4.69	6.289
Residential			10.24	8.36	9.003
TOTAL	45.47	42.02	44.91	40.91	48.608

[a] This table is included in Appendix A in English units.

[b] Includes IC engines.

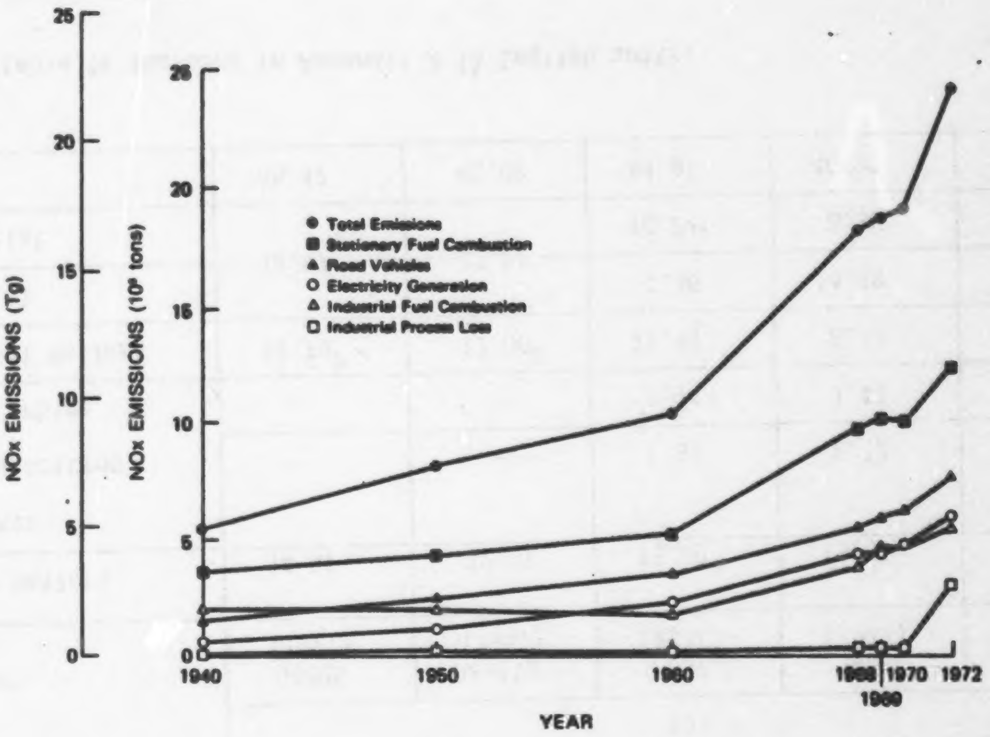


Figure 2-3. Nationwide annual NO_x emission trends 1940 – 1972 (Reference 2-37).

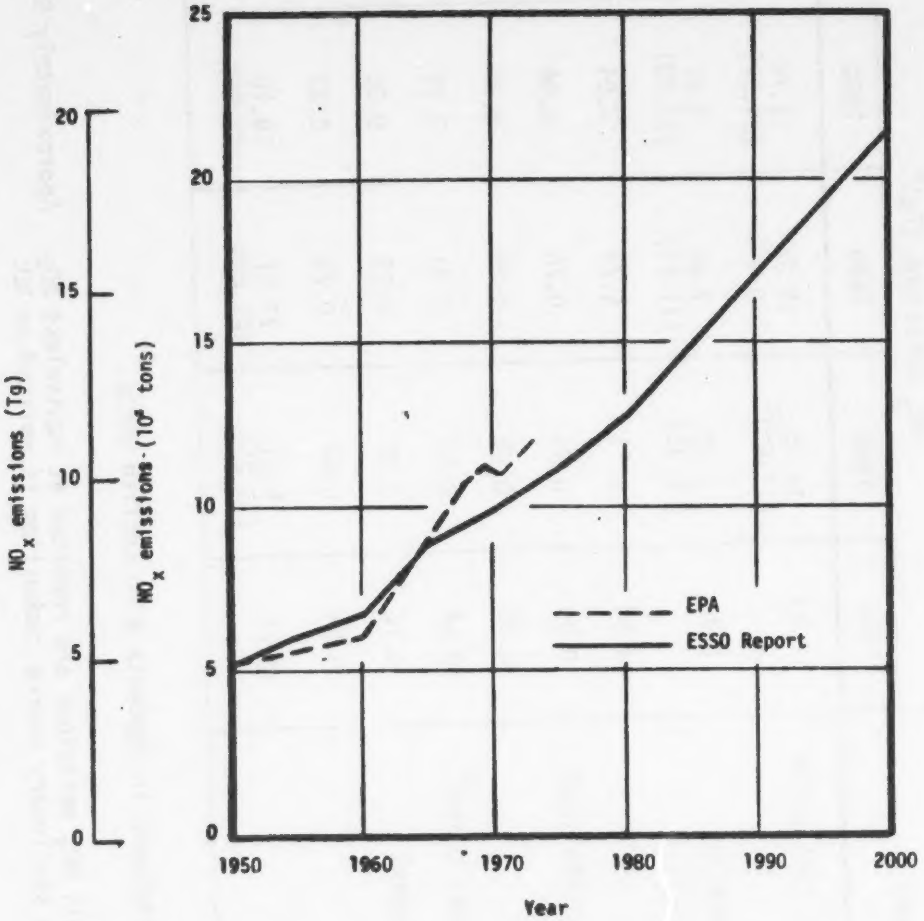


Figure 2-4. Annual stationary source NO$_x$ emission trends.

TABLE 2-26. ANNUAL NATIONWIDE NO_X EMISSIONS PROJECTED TO 2000 (Reference 2-37)[a]

Source Category	NO_x Emissions (Tg)[b]				
	1972	1980	1985	1990	2000
Stationary Fuel Combustion	11.13	14.48 (15.53)[c]	15.26 (19.44)	16.74 (24.62)	19.72 (40.32)
Electric Generation	5.39	7.40 (8.45)	7.44 (11.62)	8.05 (15.93)	9.29 (29.89)
Industrial	4.89	6.11	6.77	7.54	9.08
Commercial-Institutional	0.59	0.69	0.76	0.84	1.01
Residential	0.26	0.28	0.29	0.31	0.34
Industrial Process Losses[d]	0.64	0.86	1.03	1.25	1.68
Solid Waste Disposal	0.16	0.20	0.23	0.26	0.31
Miscellaneous	0.54	0.67	0.79	0.93	1.19
TOTAL	12.47	16.21 (17.26)	17.31 (21.49)	19.18 (27.06)	22.90 (43.50)

[a] This table is included in Appendix A in English units.

[b] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

[c] NO_x emissions for no new nuclear power plants after 1975 are given in parentheses.

[d] Industrial process losses corrected for 1972 reporting error in Reference 2-37.

- Implementation of NSPS (1972) for utility boilers and nitric acid plants
- Electrical demand grows at about 6.5 percent per year
- No increase in oil consumption after 1975
- The 1940 to 1972 growth rate of NO_x emissions from industrial, commercial, and institutional sources will be reduced over the next 30 years to 2.63 percent per year due to a shift to electricity

Two cases for electric power generation are considered. One assumes that most new electric power plants will be nuclear; the other assumes no new nuclear plants after 1975. Neither of these are realistic but were considered, at the time they were made, to bracket the possible cases. The uncertainty of projections of this nature is compounded by several emerging trends:

- There will be a significant increase in the utilization of coal in power generation, leading to an intensified NO_x problem unless stringent controls are adopted
- Industrial area sources may be switching from gas to oil or coal, resulting in larger potential NO_x emissions
- The potential application of alternate fuels is difficult to quantify at this time (probably 10 years away)
- The recent emphasis on energy conservation has produced lower than expected energy growth rates in the industrial and utility sectors

In view of these trends, the confidence level of any speculations on growth rates of specific equipment/fuel combinations is very low. Other significant factors affecting future NO_x emissions include the following:

- Major technological developments in equipment design, fuels and fuel treatment, combustion control and exhaust gas cleanup
- Uncertainty concerning the future of nuclear energy as a major source of electrical power
- The degree to which NO_x emissions will be regulated by both local and federal agencies

More recent projections of stationary source NO_x emissions have been made in Reference 2-38. Several growth and control scenarios are considered. The energy use patterns are based primarily on FEA (Reference 2-39) and ERDA (Reference 2-40) reports. Emission factors consider retirement rates of old equipment and various levels of NSPS (including existing, proposed, and possible) for

TABLE 2-27. ESTIMATED FUTURE NSPS CONTROLS (Reference 2-38)

NO_x Source		Date Implemented	Standard (ng/J)
Utility and Large Industrial Boilers (>73 MW)[a]		1971	300
	Coal	1977	258
		1981	215
		1985	172
		1988	129
	Oil	1971	129
	Gas	1971	86
Large Packaged Boilers (>7.3 MW)[a]	Coal	1979	258
		1985	215
		1990	172
	Oil	1979	86
	Gas	1979	129
Small Packaged Boilers (<7.3 MW)[a]	Coal	1979	50% reduction
	Oil	1979	86
	Gas	1979	129
Small Commercial and Residential Units	Oil	1983	30
	Gas	1983	17
Gas Turbines		1977	129
		1983	86
IC Engines	Dist Oil	1972	1390
		1985	1040
	Nat Gas	1979	1240
		1985	930
	Gasoline	1979	950
		1985	710
Process Combustion		1981	20% reduction
		1990	40% reduction

[a] Thermal input

TABLE 2-28. ANNUAL NATIONWIDE NO_X EMISSIONS TO 2000 (Reference 2-38)[a]

Source Category	NO_x Emissions (Tg)[b]				
	1974	Low Nuclear		High Nuclear	
		1985	2000	1985	2000
Electric Generation	5.566	7.410	10.104	6.420	6.026
Packaged Boilers	2.345	2.332	1.646	2.043	1.857
Internal Combustion	2.297	1.629	1.329	1.629	1.329
Warm Air Heating	0.321	0.261	0.242	0.261	0.242
Industrial Processes	0.432	0.260	0.300	0.260	0.300
Incineration	0.040	0.053	0.076	0.053	0.076
Noncombustion	0.193	0.239	0.322	0.239	0.322
TOTAL	11.194	12.184	14.019	10.905	10.152

[a] This table is included in Appendix A in English units.

[b] By convention all NO_x emissions are reported as equivalent NO_2. Approximately 95 percent of the NO_x from stationary source combustion is emitted as NO.

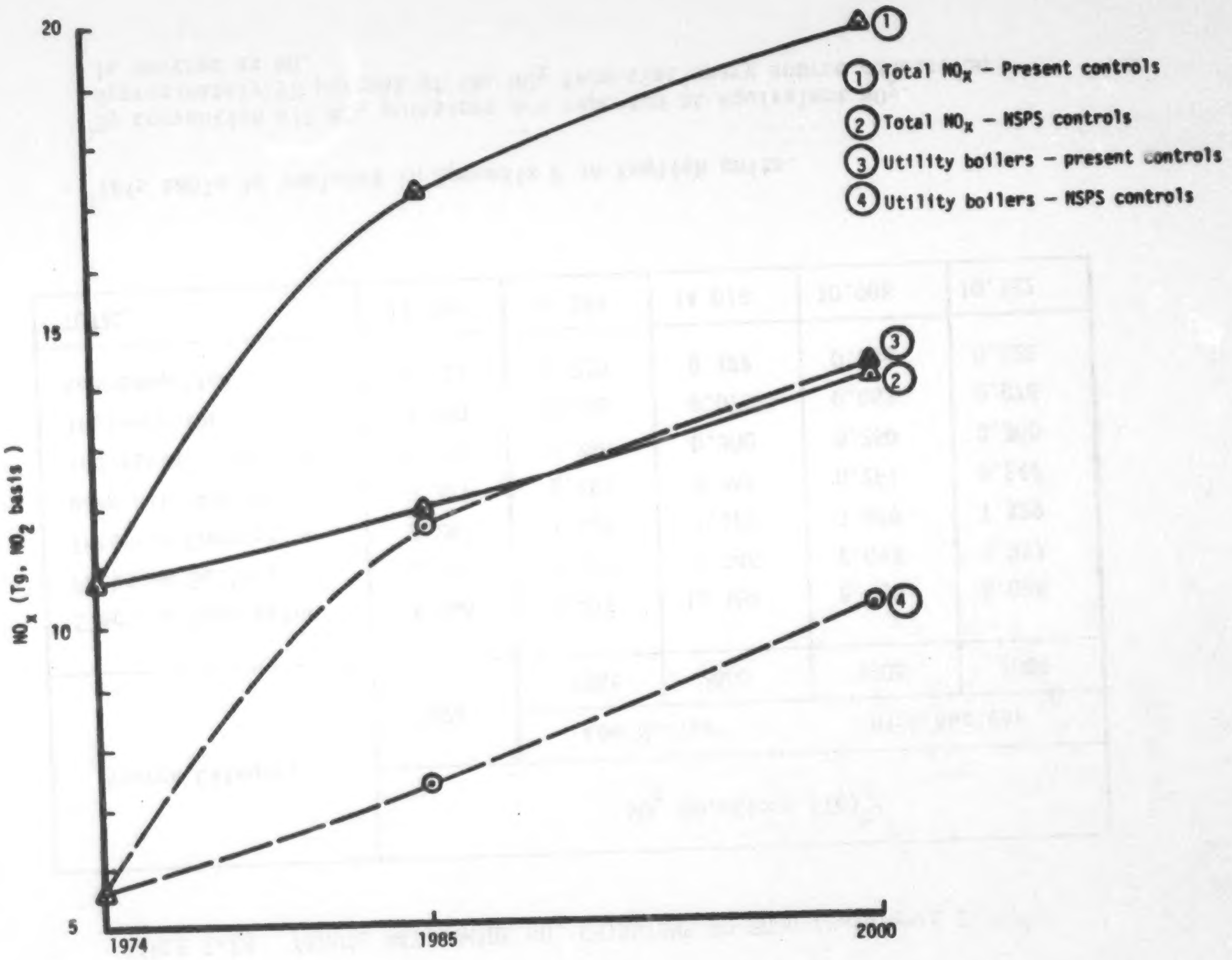


Figure 2-5. Annual stationary source NO_x emissions projections — low nuclear (Reference 2-38).

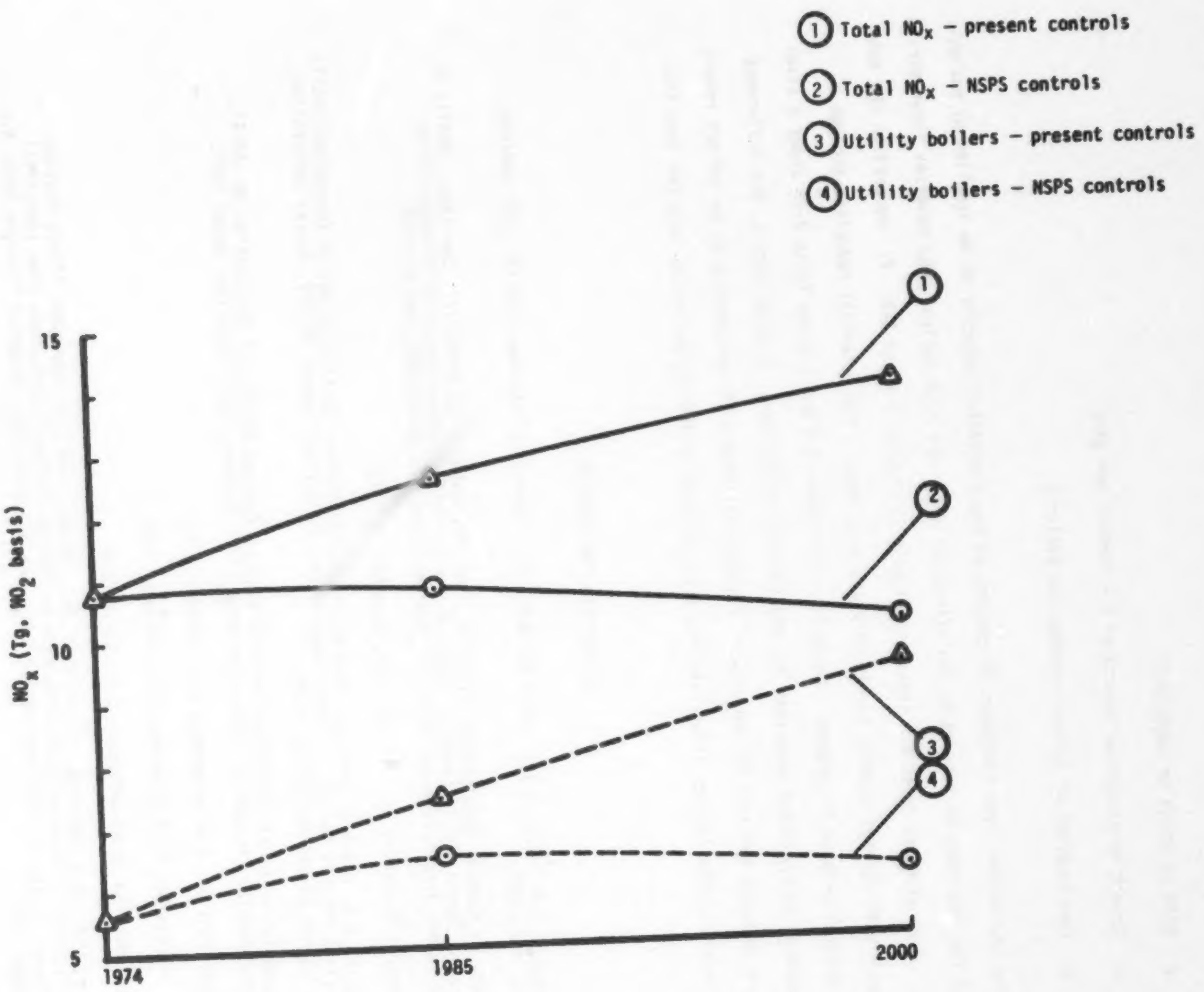


Figure 2-6. Annual stationary NO_x emissions projections – high nuclear (Reference 2-38).

new equipment. The most stringent NSPS considered are given in Table 2-27. Table 2-28 presents a breakdown by end use sector for two of the cases considered in Reference 2-38. The main assumptions are:

- NSPS as shown in Table 2-27
- Growth in electrical demand of 4.4 percent per year
- Continuation of current consumption patterns

The low nuclear case considers 35 percent of new electrical capacity to be supplied by nuclear power and the remaining 65 percent by coal-fired boilers. The high nuclear case reverses these percentages. Both of these cases are shown graphically in Figures 2-5 and 2-6. For comparison the same growth cases with current control levels only are also shown. The potential reduction through a vigorous control program is evident. Comparison of Figures 2-5 and 2-6 and Table 2-26 shows a sizeable difference in projected emissions for the various assumptions. A large part of the difference is due to a downward revision in the growth of electrical demand in Reference 2-38 to reflect recent trends. These results further illustrate the difficulty of projecting emissions very far into the future.

REFERENCES FOR SECTION 2

2-1 Chamot, E.M., D.S. Pratt, and H.W. Redfield, "Journal of the American Chemical Society," 33, 366, 1911.

2-2 Code of Federal Regulations, Title 40, Part 60, Appendix A, Method 7. See also: Hamil, H. and R. Thomas, "Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources," SwRI-EPA Contract 68-02-0626, May 8, 1974.

2-3 Federal Register, Vol. 41, No. 232, December 1, 1976.

2-4 Mason, H.B. and A.B. Shimizu, "Definition of the Maximum Stationary Source Technology (MSST) Systems Program for NO$_x$," (Draft Report) Aerotherm Final Report 74-123, Acurex Corporation, Aerotherm Division, October 1974.

2-5 "Compilation of Air Pollution Emission Factors (Second Edition)," Publication No. AP-42, Environmental Protection Agency, Research Triangle Park, North Carolina, April 1973.

2-6 Supplement No. 4 of Reference 2-5, January 1975.

2-7 Supplement No. 5 of Reference 2-5, December 1975.

2-8 Supplement No. 6 of Reference 2-5, April 1976.

2-9 Cato, G.A., H.J. Buening, C.C. DeVivo, B.C. Morton, and J.M. Robinson, "Field Testing: Application of Combustion Modification to Control Pollutant Emissions from Industrial Boilers — Phase 1," KVB Engineering Inc., EPA-650/2-74-078a, Research Triangle Park, N.C., October 1974.

2-10 Crawford, A.R., E.H. Manny, and W. Bartok, "Field Testing: Application of Combustion Modifications to Control NO$_x$ Emissions from Utility Boilers," Exxon Research and Engineering Company, June 1974.

2-11 Offen, G.R., et al., "Standard Support Document and Environmental Impact Statement — Stationary Reciprocating Internal Combustion Engines" (Draft Report). Acurex Corp./Aerotherm Division, Mountain View, California, Project 7152, March 1976.

2-12 Environmental Protection Agency, "Standard Support and Environmental Impact Statement for Standards of Performance: Lignite-Fired Steam Generators," Final Draft, OAPQS, March 1975.

2-13 "Standard Support and Environmental Impact Statement, Vol 1: Proposed Standards of Performance for Stationary Gas Turbines," EPA-450/2-77-017a, September 1977.

2-14 Personal communication with H.J. Melosh III, Foster Wheeler Corporation.

2-15 Surprenant, N.F. et. al., "Preliminary Emissions Assessment of Conventional Stationary Combustion Systems," GCA Corporation, EPA Report No. 600/2-76-046b, March 1976.

2-16 FPC News, Federal Power Commission, Washington, D.C., June 6, 1975.

2-17 Dykema, O.W., and Kemp, V.E., "Inventory of Combustion Related Emissions from Stationary Sources," (First Update). Aerospace Corporation, EPA-600/2-77-066a, March 1977.

2-18 Putnam, A.A., Kropp, E.L., and Barrett, R.E., "Evaluation of National Boiler Inventory," Battelle Columbus Laboratories, October 1975.

2-19 Personal communication with R.R. Vosper, Coen Company, January 1977.

2-20 "Current Industrial Reports, Steel Power Boilers," 1968-1975, U.S. Department of Commerce, Bureau of the Census.

2-21 "Patterns of Energy Consumption in the United States," Stock No. 4106-0034, Stanford Research Institute, Menlo Park, California, January 1972.

2-22 Dupree, W.G., and J.S. Corsentino, "Energy Through the Year 2000 (Revised)," Bureau of Mines, December 1975.

2-23 "National Gas Survey," Preliminary Draft, Federal Power Commission, 1974.

2-24 Barrett, R.E., Miller, S.E., and Locklin, D.W., "Field Investigation of Emissions from Combustion Equipment for Space Heating," Report No. EPA-R2-73-084a, Prepared by Battelle Memorial Institute, Columbus, Ohio, June 1973.

2-25 "Nationwide Inventory of Air Pollutant Emissions 1968," Pub. No. AP-73, Environmental Protection Agency, Research Triangle Park, North Carolina, July 1971.

2-26 Cavender, J.H., Kircher, D.S. and Hoffman, A.I., "Nationwide Air Pollutant Emission Trends 1940-1970," Pub. No. AP-115, Environmental Protection Agency, Research Triangle Park, North Carolina, January 1973.

2-27 Crump, L.H. and Reading, C.L., "Fuel and Energy Data – United States by States and Regions, 1972," Information Circular 8647, Bureau of Mines, Department of Interior.

2-28 "Monthly Energy Review," Federal Energy Administration, July 1976.

2-29 McGowin, C.R., "Stationary Internal Combustion Engines in the United States," Report No. EPA-R2-73-210, Prepared by Shell Development Company, Houston, Texas, April 1973.

2-30 Foley, G., "Industrial Growth Forecasts," Stanford Research Institute, Contract No. 68-02-1320, September 1974.

2-31 Bartok, W., et. al., "Systems Study of Nitrogen Oxide Control Methods for Stationary Sources – Vol. II," prepared for National Air Pollution Control Administration, NTIS Report No. PB-192-789, Esso Research and Engineering, 1969.

2-32 "OAQPS Data File of Nationwide Emissions, 1971," Office of Air Quality Planning and Standards, Environmental Protection Agency, May 1973.

2-33 Goldish, J. et. al., "Systems Study of Conventional Combustion Sources in the Iron and Steel Industry," Report No. EPA R2-73-192, Prepared by Walden Research Corporation, Cambridge, Massachusetts, April 1973.

2-34 Oil and Gas Journal, Volume 73, No. 12. The Petroleum Publishing Company, Tulsa, Oklahoma.

2-35 "Annual Survey of Manufacturers 1974 – Fuels and Electric Energy Consumed," U.S. Department of Commerce, Bureau of the Census.

2-36 Ketels, P.A., J.D. Nesbitt, and R.D. Oberle, "A Survey of Emissions Control and Combustion Equipment Data in Industrial Process Heating," Institute of Gas Technology, Final Report 8949, October 1976.

2-37 National Academy of Science, "Air Quality and Stationary Source Emission Control," Prepared for the Committee on Public Works, United States Senate, Serial No. 94-4, March 1975.

2-38 Salvesen, K.G., et al., "Emissions Characterization of Stationary NO_x Sources," Aerotherm Draft Report, TR-77-72, October 1977.

2-39 "1976 National Energy Outlook," Federal Energy Administration, FEA/N-75/713, February 1976.

2-40 "A National Plan for Energy Research, Development & Demonstration: Creating Energy Choices for the Future," ERDA-48, Volume 2 of 2.

SECTION 3

CONTROL TECHNIQUES

This section presents a survey of the general principles and developmental status of potential techniques for NO_x control for stationary sources. It is intended to provide a broad perspective on the various suggested concepts for NO_x control by combustion process modification and flue gas treatment for combustion sources and by tail gas cleanup for noncombustion sources. A more detailed review of the effectiveness and cost of control implementation on specific equipment types is given in Sections 4, 5, and 6.

3.1 COMBUSTION MODIFICATIONS

Modifying the combustion process is the most widely used technique for reducing combustion generated oxides of nitrogen. This section describes the four most popular methods: modification of the operating conditions, equipment design modification, fuel modification, and use of alternate combustion processes. The section begins by describing the factors which affect the generation of NO_x during combustion.

3.1.1 Factors Affecting NO_x Emissions from Combustion

Oxides of nitrogen formed in combustion processes are usually due either to thermal fixation of atmospheric nitrogen in the combustion air, leading to "thermal NO_x", or to the conversion of chemically bound nitrogen in the fuel, leading to "fuel NO_x". For natural gas and light distillate oil firing, nearly all NO_x emissions result from thermal fixation. With residual oil, crude oil, and coal, the contribution from fuel-bound nitrogen can be significant and, under certain operating conditions, predominant.

A third potential mechanism of NO_x formation arises in processes such as glass manufacturing, where the raw materials in contact with the combustion products contain nitrogen compounds. Little is known about the extent of conversion to NO_x of these nitrogen compounds, or of the effects of combustion modifications on this mechanism.

3.1.1.1 Thermal NO_x

The detailed chemical mechanism by which molecular nitrogen in the combustion air is converted to nitric oxide is not fully understood. In practical combustion equipment, particularly for liquid or solid fuels, the kinetics of the N_2-O_2 system are coupled to the kinetics of hydrocarbon oxidation and both are influenced, if not dominated, by effects of turbulent mixing in the flame zone. It is, however, generally accepted that thermal NO_x forms at high temperatures in an excess of air. The usually stable oxygen molecule dissociates to oxygen atoms which are very reactive. These atoms react with the otherwise stable nitrogen molecule to form NO_x.

The most widely accepted reactions that describe the formation of thermal NO_x are those of the extended form of the Zeldovich chain mechanism (Reference 3-1):

$$O_2 + M \rightleftarrows O + O + M \qquad (3\text{-}1)$$

$$N_2 + O \rightleftarrows NO + N \qquad (3\text{-}2)$$

$$N + OH \rightleftarrows NO + H \qquad (3\text{-}3)$$

$$O_2 + N \rightleftarrows NO + O \qquad (3\text{-}4)$$

Equation (3-1) is considered to be in equilibrium, and M is a "third body", normally taken to be molecular nitrogen. For thermal NO_x, reaction (3-2) is much slower than reaction (3-3) and, therefore, controls the rate of NO formation. The creation of an NO molecule from reaction (3-2) is accompanied by the release of an N atom, which rapidly forms another NO molecule from reaction (3-3) and (3-4). Reactions (3-2) and (3-4) are the chain-making and chain-breaking mechanisms, and the oxygen atom is the chain carrier.

Experimental measurements of NO formation in heated mixtures of N_2, O_2 and Argon at atmospheric pressure have been correlated with an equation of the form (Reference 3-2):

$$[NO] = k_1 e^{-k_2/T} [N_2] [O_2]^{1/2} t \qquad (3\text{-}5)$$

Where: [] = mole fraction

T = absolute temperature

t = residence time

k_1, k_2 = constants

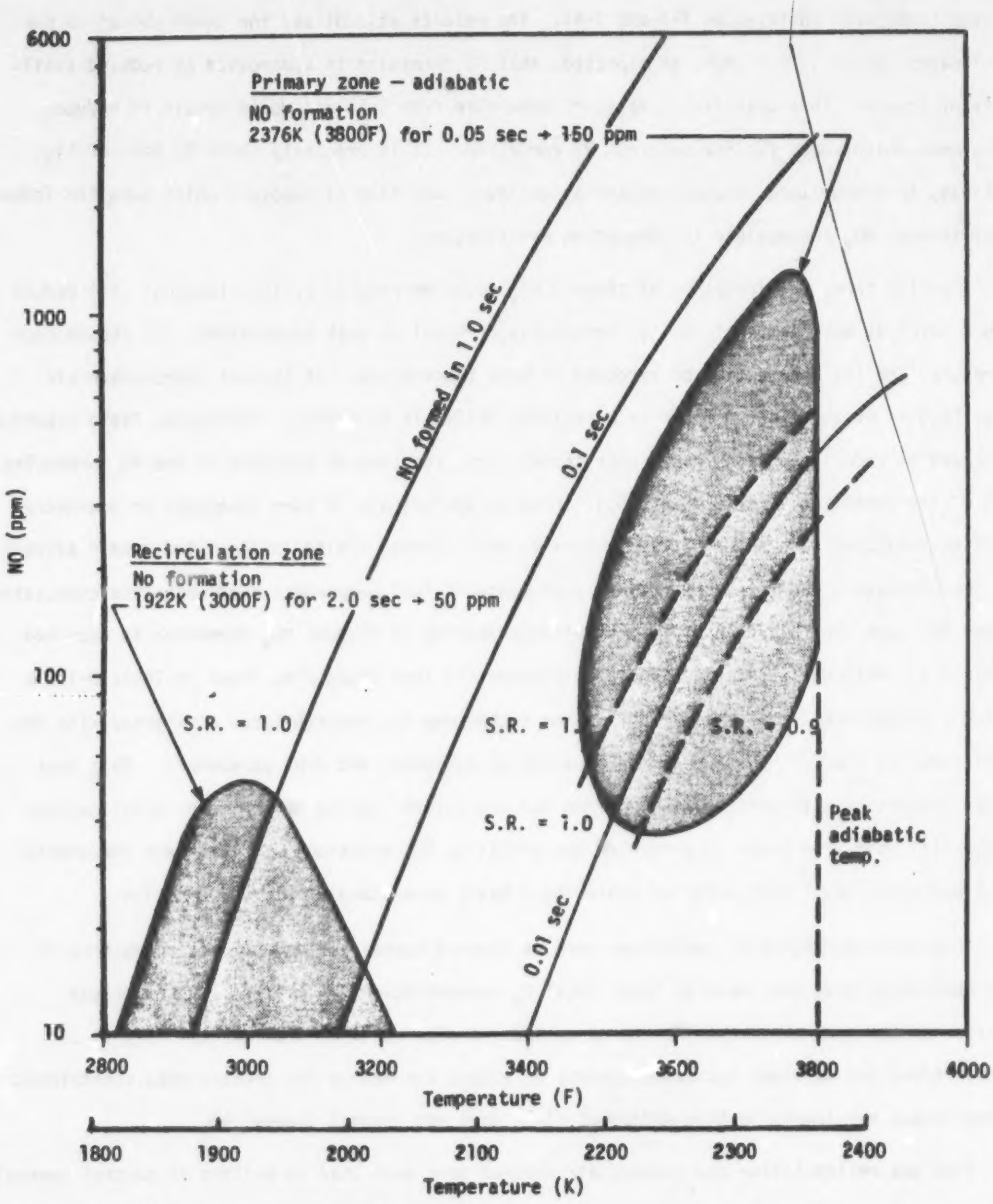
This expression reflects the strong dependence of NO formation on temperature. It also shows that NO concentration is directly proportional to N_2 concentration and to the residence time, and varies with O_2 to the one-half power. A rate expression such as this one does not fully describe the thermal NO_x reaction mechanism, but it does give some valuable qualitative trends.

The temperature and time dependencies of NO formation are illustrated in Figure 3-1 for idealized conditions (References 3-3 and 3-4). The results at 0.01 sec for three values of the stoichiometric ratio (S.R.) show, as expected, that NO formation is suppressed by reduced availability of oxygen. In a practical combustor, departure from S.R. = 1 would result in reduced temperatures which would further suppress NO formation. It is precisely these factors of high sensitivity to temperature, oxygen concentration level, and time of exposure which make the formation of thermal NO_x susceptible to combustion modification.

Ideally, then, the formation of thermal NO_x could be reduced by four tactics: (1) reduce nitrogen level at peak temperature, (2) reduce oxygen level at peak temperature, (3) reduce peak temperature, and (4) reduce time of exposure at peak temperature. In typical hydrocarbon-air flames, $[N_2]$ is of the order 0.7 and is relatively difficult to modify. Therefore, field practice has focused on reducing oxygen level, peak temperature, and time of exposure in the NO_x-producing region of the combustor. (Reference 3-5.) These parameters are in turn dependent on secondary combustion variables such as combustion intensity and internal mixing in the flame zone - effects which are ultimately determined by primary equipment and fuel parameters over which the combustion engineer has some control. A hierarchy of effects leading to thermal NO_x formation is depicted in Table 3-1. Although causal relationships between the four categories shown in Table 3-1 are not firmly established, combustion modification technology is, nevertheless, confronted with the task of reducing thermal NO_x through modification of equipment and fuel parameters. This task has been approached with efforts ranging from the short-term testing of equipment modifications on commercial units, in order to determine the effect on NO_x emissions, to long-term fundamental studies and pilot testing directed at achieving a basic understanding of NO_x formation.

Combustion modification techniques such as lowered excess air and off stoichiometric or staged combustion have been used to lower local O_2 concentrations in boilers. Also, staged combustion in the form of stratified charge cylinder design has been used successfully in IC engines. Since gas turbines typically operate at excess air levels far greater than stoichiometric, lowering excess air levels in this equipment class does not control thermal NO_x.

Flue gas recirculation and reduced air preheat have been used in boilers to control thermal NO_x by lowering peak flame temperatures. Analogously, exhaust gas recirculation (EGR), reduced manifold air temperature (IC engines) and reduced air preheat (regenerative gas turbines) have been



*S.R. — stoichiometric ratio

Figure 3-1. Kinetic formation of nitric oxide for combustion of natural gas atmospheric pressure (References 3-3 and 3-4).

TABLE 3-1. FACTORS CONTROLLING THE FORMATION OF THERMAL NO_x

Primary Equipment and Fuel Parameters	Combustion Parameters	Fundamental Parameters	
Inlet temperature, velocity Firebox design Fuel composition Injection pattern of fuel & air Size of droplets or particles Burner swirl External mass addition	Combustion intensity Heat removal rate Mixing of combustion products into flame Local fuel-air ratio Turbulent distortion of flame zone	Oxygen level Peak temp. Exposure time at peak temp.	Thermal NO_x

applied to IC engines and gas turbines. Other techniques designed to lower peak temperatures in prime movers include water injection and altered air/fuel ratios.

Techniques which reduce residence time at peak temperature have been more easily applied to prime mover equipment classes. Although flue gas recirculation (and EGR) reduces combustion gas residence time, it acts as a thermal NO_x control primarily through temperature reduction. Techniques which specifically reduce exposure time at high temperatures include ignition retard for IC engines and early quench with secondary air for gas turbines.

It is important to recognize that the above-mentioned techniques for thermal NO_x reduction alter combustion conditions on a macroscopic scale. Although these macroscopic techniques have all been relatively successful in reducing thermal NO_x, local microscopic combustion conditions ultimately determine the amount of thermal NO_x formed. For example, recent studies on the formation of thermal NO in gaseous flames have confirmed that internal mixing can have large effects on the total amount of NO formed (References 3-6, 3-7). Burner swirl, combustion air velocity, fuel injection angle and velocity, burner divergent angle and confinement ratio all affect the mixing between fuel, combustion air and recirculated products. Mixing, in turn, alters the local temperatures and species concentrations which control the rate of NO_x formation.

Unfortunately, generalizing these effects is difficult, because the interactions are complex. Increasing swirl, for example, may both increase entrainment of cooled combustion products (hence lowering peak temperatures) and increase fuel/air mixing (raising local combustion intensity). The net effect of increasing swirl can be to either raise or lower NO_x emissions, depending on other system parameters.

In summary, a hierarchy of effects depicted in Table 3-1 produces local combustion conditions which promote thermal NO_x formation. Although combustion modification technology seeks to affect the fundamental parameters of combustion, modifications must be made by changing the primary equipment and fuel parameters. Control of thermal NO_x, which began by altering inlet conditions and external mass addition, has moved to more fundamental changes in combustion equipment design.

3.1.1.2 Fuel NO_x

The role of fuel-bound nitrogen as a source of NO_x emissions from combustion sources has been recognized since 1968 (Reference 3-8). Although the relative contribution of fuel and thermal NO_x to total NO_x emissions from sources firing nitrogen-containing fuels has not been definitively established, recent estimates indicate that fuel NO_x is significant and may even predominate. In one recent study (Reference 3-9), residual oil and pulverized coal were burned in an argon/oxygen mixture to eliminate thermal NO_x effects. Results show that fuel NO_x can account for over 50 percent of total NO_x production from residual oil firing and approximately 80 percent of total NO_x from coal firing. Therefore, as coal is increasingly used as a national energy source, the control of fuel NO_x will become more important.

Fuel-bound nitrogen occurs in coal and petroleum fuels. The nitrogen containing compounds in petroleum tend to concentrate in the heavy resin and asphalt fractions upon distillation (Reference 3-10). Table 3-2 gives analyses of typical fuel oils. Fuel nitrogen is less than 0.01 percent for distillate oils; however, it ranges from 0.1 to 0.5 for residual oils.

The classes of nitrogen compounds in fuel oil include indoles, quinolines, pyradines, and carbazoles. Their quantities in the distilled fractions vary with the origin of the crude oil. From one California crude, pyradines dominated in the distillate fraction and carbazoles dominated in residual oil (Reference 3-11).

Table 3-3 gives analyses of four ranks of U.S. coals. Nitrogen content of most U.S. coals lies in the 0.5 to 2 percent range (Reference 3-12); anthracite coals contain the least and bituminous coals the most nitrogen. Although the structure of coal is not known with certainty, it is believed that coal-bound nitrogen occurs in aromatic ring structures such as pyridine, picoline, quinoline, and nicotine (Reference 3-10). Figure 3-2 illustrates the nitrogen content of various U.S. coals, expressed as ng NO_2 produced per Joule for 100 percent conversion of the fuel nitrogen. The figure clearly shows that if all coal-bound nitrogen were converted to NO_x, emissions for all coals would exceed New Source Performance Standards. Fortunately, only a fraction of the fuel nitrogen is converted to NO_x for both oil and coal firing, as shown in Figure 3-3. Furthermore, the figure indicates that fuel nitrogen conversion decreases as nitrogen content increases. Thus, although fuel NO_x emissions undoubtedly increase with increasing fuel nitrogen content, the emissions increase is not proportional. In fact, recent data indicate only a small increase in NO_x emissions as fuel nitrogen increases (Reference 3-14). From observations such as these, the effectiveness of partial fuel denitrification as a NO_x control method seems doubtful.

The precise mechanism by which fuel nitrogen is converted to NO_x is not understood; however, certain aspects are clear, particularly for coal combustion. In a large, pulverized coal utility boiler, the coal particles are conveyed by an airstream into the hot combustion chamber, where they are heated at a rate in excess of 10^4K/s. Almost immediately volatile species, containing some of the coal-bound nitrogen, vaporize and burn homogeneously, rapidly (~10 ms) and probably detached from the original coal particle. Combustion of the remaining solid char is heterogeneous and much slower (~300 ms).

TABLE 3-2. ANALYSES OF TYPICAL U.S. FUEL OILS (Reference 3-12)

	Distillate Oil		Residual Oil		
	No. 1	No. 2	No. 4	No. 5	No. 6
Specific gravity (°API)	0.84-0.81 (35-42)	0.88-0.84 (30-35)	0.910-0.904 (23-25)	0.946-0.922 (18-22)	0.986-0.959 (12-16)
Viscosity, mm^2/s (Saybolt sec.)	-	2.0-3.5 (33-37)	6-26 (45-125)	32-151 (150-700)	195-1948 (900-9000)
Heating value, kJ/g (10^3 Btu/gal)	45.6-46.1 (132.7-136.2)	44.5-45.8 (136.2-139.7)	42.4-45.0 (149.8-144.0)	42.0-44.1 (144.6-147.2)	40.4-44.1 (148.4-151.0)
Sulfur, wt%	0.1-0.3	0.2-0.8	1-3	1-3	1-5
Hydrogen, wt%	12-14	12-14	11-12	10-12	10-12
Carbon, wt%	86-88	86-88	86-88	86-88	85-88
Ash, wt%	0.01	0.01	0.01-0.1	0.01-0.1	0.01-0.3
Nitrogen, wt%	<0.01	<0.01	0.1-0.5	0.1-0.5	0.1-0.5
Nitrogen, μg/J of fuel (lb/10^3 Btu)	<0.22 (<0.51)	<0.22 (<0.51)	2.4-11.7 (5.6-27.2)	2.4-12.0 (5.6-27.9)	2.5-12.4 (5.8-28.8)

TABLE 3-3. ANALYSES OF TYPICAL U.S. COALS AND LIGNITE (Reference 3-12)

Analysis	Anthracite	Bituminous	Sub-bituminous	Lignite
Moisture, wt%	2-5	2-15	15-30	25-45
Volatile matter, wt%	5-12	18-40	30-40	25-30
Fixed carbon, wt%	70-90	40-75	35-45	20-30
Ash, wt%	8-20	3-25	3-25	5-30
Heating value, kJ/g (1000 Btu/lb)	27.8-33.6 (11.9-14.4)	23.2-32.5 (10.0-14.0)	18.6-24.4 (8.0-10.5)	12.8-18.6 (5.5-8.0)
Sulfur, wt%	<1	0.5-5	1.5-3	0.5-2.5
Nitrogen, wt%	0.5-1	1-2	1-1.5	0.5-1.5
Nitrogen, µg/J of fuel ($lb/10^6$ Btu)	180-360 (0.42-0.84)	430-860 (1.00-2.00)	540-810 (1.26-1.88)	390-1170 (0.91-2.72)

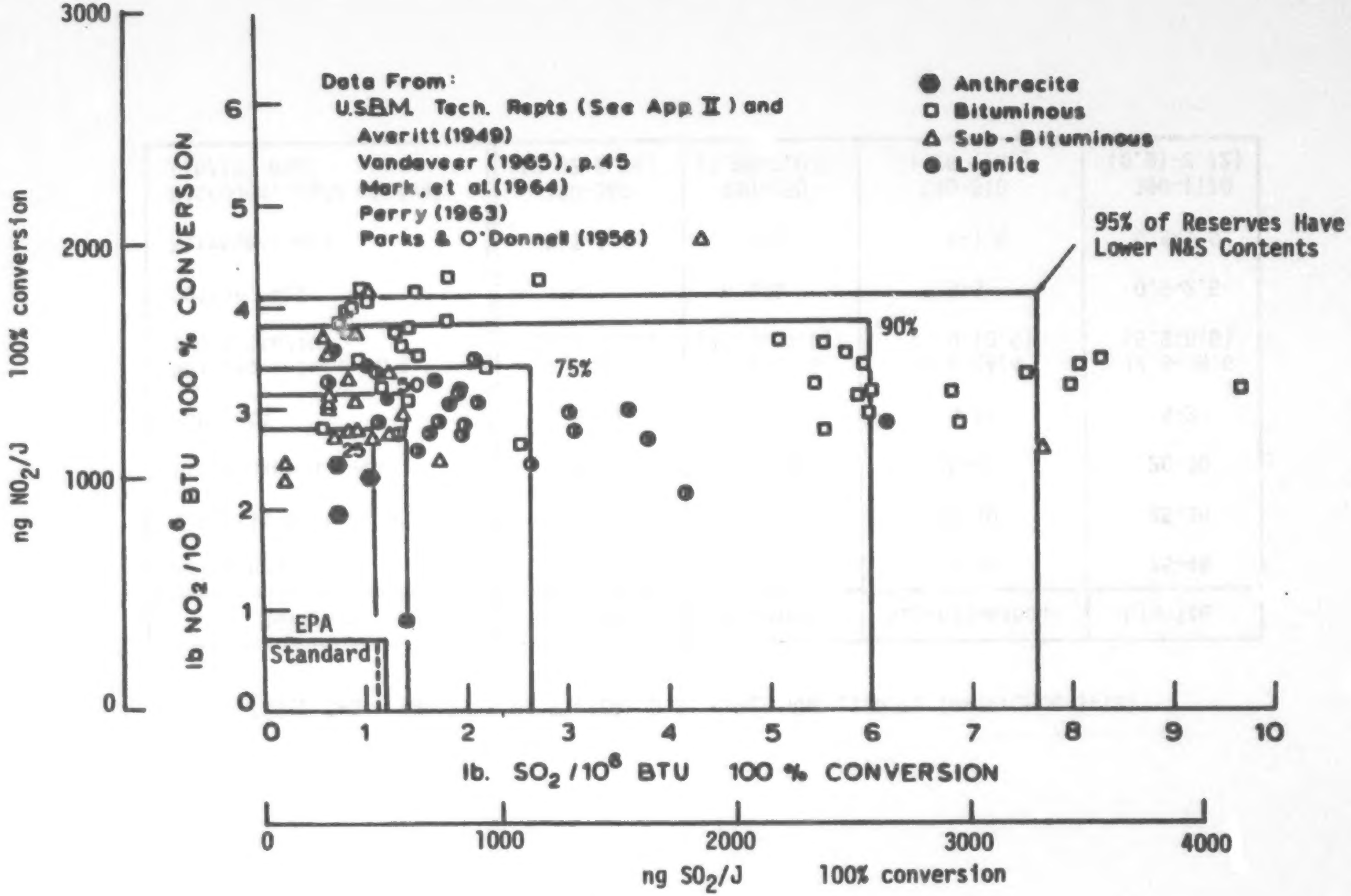


Figure 3-2. Nitrogen and sulfur content of U.S. coal reserves (Reference 3-13).

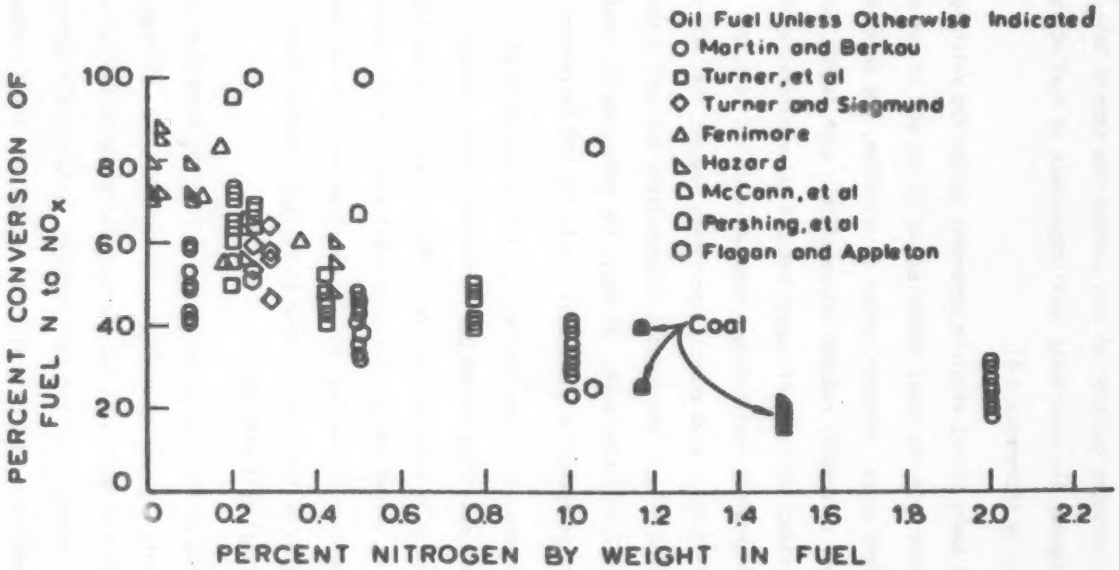


Figure 3-3. Percent conversion of fuel nitrogen to NO_x in laboratory scale combustion (Reference 3-13).

Figure 3-4 summarizes what may happen to fuel nitrogen during this process. In general, nitrogen evolution parallels evolution of the total volatiles, except during the initial 10 to 15 percent volatilization in which little nitrogen is released (Reference 3-16). Both total mass volatilized and total nitrogen volatilized increase with higher pryolysis temperature; the nitrogen volatilization increases more rapidly than that of the total mass. Total mass volatilized appears to be a stronger function of coal composition than is total nitrogen volatilized (Reference 3-17). This supports the relatively small dependence of fuel NO_x on coal composition observed in small scale testing (Reference 3-9).

Although there is not absolute agreement on how the volatiles separate into species, it appears that about half the total volatiles and 85 percent of the nitrogeneous species do not evolve as permanent light gases. However, prior to oxidation, the devolatilized nitrogen may be converted to a small number of common, reduced intermediates, such as HCN and NH_3, in the fuel regions of the flame. The existence of a set of common reduced intermediates would explain the observations that the form of the original fuel nitrogen compound does not influence its conversion to NO (e.g., References 3-10, 3-18). More recent experiments suggest that HCN is the predominant reduced intermediate (Reference 3-19). The reduced intermediates are then either oxidized to NO, or converted to N_2 in the post-combustion zone. Although the mechanism for these conversions is not presently known, one proposed mechanism postulates a role for NCO (Reference 3-20).

Nitrogen retained in the char may also be oxidized to NO, or reduced to N_2 through heterogeneous reactions occurring in the post-combustion zone. However, it is clear that the conversion of char nitrogen to NO proceeds much more slowly than the conversion of devolatilized nitrogen. In fact, based on a combination of experimental and empirical modeling studies, it is now believed that 60 to 80 percent of the fuel NO_x results from volatile nitrogen oxidation (References 3-16 and 3-21). Conversion of the char nitrogen to NO is in general lower, by factors of two to three, than conversion of total coal nitrogen.

Regardless of the precise mechanism of fuel NO_x formation, several general trends are evident, particularly for coal combustion. As expected, fuel nitrogen conversion to NO is highly dependent on the fuel/air ratio for the range existing in typical combustion equipment, as shown in Figure 3-5. Oxidation of the char nitrogen is relatively insensitive to fuel/air changes, but volatile NO formation is strongly affected by fuel/air ratio changes.

In contrast to thermal NO_x, fuel NO_x production is relatively insensitive to small changes in combustion zone temperature (Reference 3-18). Char nitrogen oxidation appears to be a very

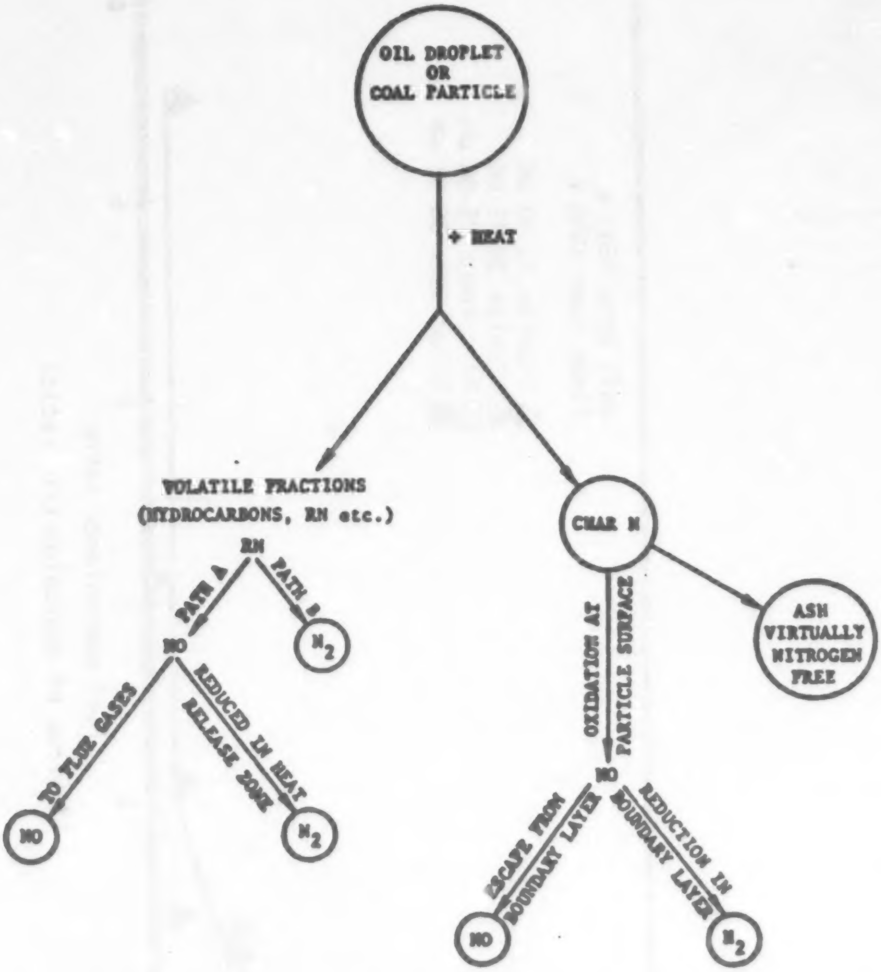

OIL DROPLET OR COAL PARTICLE
+ HEAT
VOLATILE FRACTIONS (HYDROCARBONS, RN etc.)
RN
PATH A
PATH B
N_2
NO
TO FLUE GASES
REDUCED IN HEAT RELEASE ZONE
NO
N_2
CHAR N
OXIDATION AT PARTICLE SURFACE
ASH VIRTUALLY NITROGEN FREE
NO
ESCAPE FROM BOUNDARY LAYER
REDUCTION IN BOUNDARY LAYER
NO
N_2

Figure 3-4. Possible fate of fuel nitrogen contained in coal particles or oil droplets during combustion (Reference 3-15).

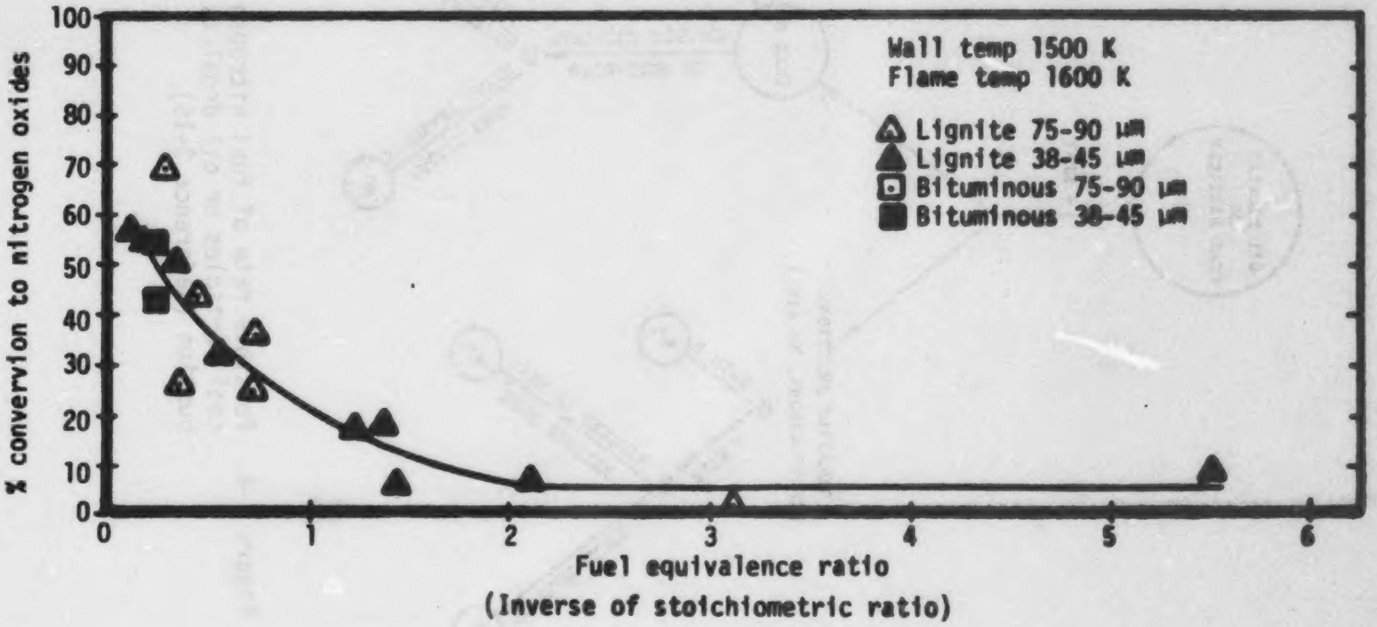


Figure 3-5. Conversion of nitrogen in coal to NO_x (Reference 3-22).

weak function of temperature, and although the amount of nitrogen volatiles appears to increase as temperature increases, this is believed to be partially offset by a decrease in percentage conversion. Furthermore, operating restrictions severely limit the magnitude of actual temperature changes attainable in current systems.

As described above, fuel NO emissions are a strong function of fuel/air mixing. In general, any change which increases the mixing between the fuel and air during coal devolatilization will dramatically increase volatile nitrogen conversion and increase fuel NO. In contrast, char NO formation is only weakly dependent on initial mixing and therefore may represent a lower limit on the emission level which can be achieved through burner modifications.

From the above modifications, it appears that, in principle, the best strategy for fuel NO_x abatement combines low excess air firing, optimum burner design, two-stage combustion and high air preheat. Assuming suitable stage separation, low excess air may have little effect on fuel NO, but it increases system efficiency. Before using LEA firing, the need to get good carbon burnout and low CO emissions must be considered.

Optimum burner design ensures locally fuel-rich conditions during devolatilization, which promotes reduction of devolatilized nitrogen to N_2. Two-stage combustion produces overall fuel-rich conditions during the first 1 to 2 seconds and promotes the reduction of NO to N_2 through reburning reactions. High secondary air preheat also appears desirable, because it promotes more complete nitrogen devolatilization in the fuel-rich initial combustion stage. This leaves less char nitrogen to be subsequently oxidized in the fuel-lean second stage. Unfortunately, it also tends to favor thermal NO formation, and at present there is no general agreement on which effect dominates.

3.1.1.3 Summary of Process Modification Concepts

In summary of the above discussion, both thermal and fuel NO_x are kinetically or aerodynamically limited in that their emission rates are far below the levels which would prevail at equilibrium. Thus, the rate of formation of both thermal and fuel NO_x is dominated by combustion conditions and is amenable to suppression through combustion process modifications. Although the mechanisms are different, both thermal and fuel NO_x are promoted by rapid mixing of oxygen with the fuel. Additionally, thermal NO_x is greatly increased by long residence time at high temperature. The modified combustion conditions and control concepts which have been tried or suggested to combat the formation mechanisms are as follows:

- Decrease primary flame zone O_2 level by
  - Decreased overall O_2 level
  - Controlled mixing of fuel and air
  - Use of fuel-rich primary flame zone

- Decrease time of exposure at high temperature by
  - Decreased peak temperature:
    - Decreased adiabatic flame temperature through dilution
    - Decreased combustion intensity
    - Increased flame cooling
    - Controlled mixing of fuel and air or use of fuel-rich primary flame zone
  - Decreased primary flame zone residence time
- Chemically reduce NO_x in post-flame region by
  - Injection of reducing agent

Table 3-4 relates these control concepts to applicable combustion process modifications and equipment types. The process modifications are further categorized according to their role in the control development sequence: operational adjustments, hardware modifications of existing equipment or through factory installed controls, and, major redesigns of new equipment. The controls for decreased O_2 are also generally effective for peak temperature reduction but have not been repeated. The following subsections review the status of each of the applicable controls.

3.1.2 Modification of Operating Conditions

The modification techniques described in this subsection include low excess air, off stoichiometric combustion, flue gas recirculation, reduced air preheat, load reduction, steam or water injection, and ammonia injection.

3.1.2.1 Low Excess Air Combustion

Reducing the total amount of excess air supplied for combustion is an effective demonstrated method for reducing NO_x emissions from utility and industrial boilers, residential and commercial furnaces, warm air furnaces, and process furnaces. Low excess air (LEA) firing reduces the local flame zone concentration of oxygen, thus reducing both thermal and fuel NO_x formation. LEA firing is furthermore easy to implement and increases efficiency (slight decrease in fuel consumption). It is, therefore, used extensively in both new and retrofit applications, either singly or in combination with other control measures. The ultimate level of excess air is generally limited by the onset of smoke or carbon monoxide emissions which occurs when excess air is reduced to levels far below the design conditions. Fouling and slagging may also increase in heavy oil- or coal-fired applications at very low levels of excess air, thus limiting the potential of this technique.

Low excess air firing is the most widespread NO_x control technique for utility boilers. It was initially implemented to increase thermal efficiency and reduce stack gas opacity due to acid mist. A number of studies have shown LEA firing to be effective in reducing NO_x emissions without

TABLE 3-4: SUMMARY OF COMBUSTION PROCESS MODIFICATION CONCEPTS

Combustion Conditions	Control Concept	Applicable Equipment	Effect on Thermal NO_x	Effect on Fuel NO_x	Primary Applicable Controls		
					Operational Adjustments	Hardware Modification	Major Redesign
Decrease primary flame zone O_2 level	Decrease overall O_2 level	Boilers, furnaces	Reduces O_2-rich, high-NO_x pockets in the flame	Reduces exposure of fuel nitrogen intermediaries to O_2	Low excess air firing	Flue gas recirculation (FGR)	
	Delayed mixing of fuel and air	Boiler, furnaces	Flame cooling and dilution during delayed mix reduces peak temp.	Volatile fuel N reduces to N_2 in the absence of oxygen	Burner adjustments	Low NO_x burners	Optimum burner/firebox design
	Increased fuel/air mixing	Gas turbines	Reduces local hot stoichiometric regions in overall fuel lean combustion	Increases			New can design; premix, prevap.
	Primary fuel-rich flame zone	Boilers, furnaces, IC	Flame cooling in low-O_2, low-temp. primary zone reduces peak temp.	Volatile fuel N reduces to N_2 in the absence of oxygen	Burners out of service; biased burner firing	Overfire air ports, stratified charge	Burner/firebox design for two-stage combustion
Decrease peak flame temperature	Decrease adiabatic flame temperature	Boilers, furnaces, IC, gas turbines	Direct supression of thermal NO_x mechanism	Ineffective	Reduced air preheat	Water injection, FGR	
	Decrease combustion intensity	Boilers, furnaces	Increased flame zone cooling yields lower peak temp.	Minor direct effect; indirect effect on mixing	Load reduction		Enlarged firebox increased burner spacing
	Increased flame zone cooling/reduce residence time	Boilers, furnaces	Increased flame zone cooling yields lower peak temp.	Ineffective			Redesign heat transfer surfaces, firebox aerodynamics
Chemically reduce NO_x in post-flame region	Inject reducing agent	Boilers, furnaces				Ammonia injection possible on some units	Redesign convective section for NH_3 injection

significantly increasing CO or smoke levels (References 3-14, 3-23 through 3-27). NO_x reductions averaging between 16 and 20 percent are achieved on gas- and oil-fired boilers when the excess air is reduced to levels between 2 and 7 percent. Low excess air firing below 5 percent is now standard practice on most oil and gas utility boilers. NO_x reductions of 20 percent on the average are achieved on coal-fired utility boilers when excess air is reduced to the 20 percent level or lower. However, the minimum excess air levels achievable with satisfactory performance are 8 to 12 percent. In some existing units, excess air levels below 15 to 18 percent present operating problems (Reference 3-25).

The minimum practical level of excess air which can be achieved in existing boilers, without encountering operational problems, depends upon factors in addition to the type of fuel fired. These factors include low load operation, nonuniformity of air/fuel ratio, fuel and air control lags during load swings, use of upward burner tilt to increase steam superheat (for tangentially-fired boilers), and coal quality variation and ash slagging potential (for coal-fired boilers). They tend to increase the minimum excess air level at which the boiler can operate safely.

Other factors such as secondary air register settings and steam temperature control flexibility also affect the excess air levels. The boiler combustion control system must be modified so that the proportioning of fuel and air is adequate under all operating conditions. Uniform distribution of fuel and air to all burners is increasingly important as excess air is lowered. Excess air levels are also affected if other NO_x control techniques are employed. Staging and operating at reduced load increases the minimum excess air levels whereas switching from eastern to western coals could decrease the levels (References 3-24, 3-28, and 3-29).

LEA firing is a very effective method for controlling NO_x in industrial boilers. Although it is not in widespread use as a NO_x control technique for industrial boilers, LEA is generally considered as part of an energy conservation program. LEA is also a feasible NO_x control technique for residential and commercial furnaces; however, the trend in NO_x control for these sources has been in improved burner design in order to obtain low excess air levels without extensive CO emissions.

LEA is not a very promising technique for IC engines and gas turbines. When the air/fuel ratio is reduced, CO and HC emissions increase sharply for IC engines. In gas turbines, the overall air/fuel ratio cannot be modified to control NO_x, since the ratio is determined by the turbine inlet temperature.

In summary, changing the overall air/fuel ratio to control NO_x emissions is a simple, feasible, and effective technique for stationary sources of combustion, with the exception of gas turbine engines and IC engines. For certain applications such as utility boilers, LEA firing is presently considered a routine operating procedure and is incorporated in all new units. Since it is efficient and easy to implement, LEA firing will see increasingly widespread use in other applications. Most sources will require additional control methods, in conjunction with LEA, to bring NO_x emissions within statutory limits. In such cases, the extent to which excess air can be lowered will depend upon the other control techniques employed. However, virtually all developmental programs for advanced NO_x controls are placing maximum emphasis on operation at minimum levels of excess air. LEA will thus be an integral part of nearly all combustion modification NO_x controls, both current and emerging.

3.1.2.2 Off-Stoichiometric Combustion

Off-stoichiometric combustion (OSC) is a NO_x control technique in which the mixing of fuel with the combustion air is altered so that substoichiometric conditions prevail locally in the primary combustion zone. Complete combustion occurs downstream of the primary zone. OSC is effective for retrofit implementation on large boilers having multiple burners arranged in rectangular matrices mounted either on one boiler wall (front-fired) or on opposite walls (horizontally opposed-fired). This method can also be used on corner-fired boilers (tangentially fired), however in the case of OSC with burners out of service these boilers require that all four burners on any level be "taken out" simultaneously. Front-wall and horizontally opposed firing types are more flexible in the location and number of burners that can be set on air only. For new units, OSC is an attractive control technique to be included in the design of both single and multiple burner units of all design types.

Off-stoichiometric combustion appears to be an effective technique for control of both thermal and fuel NO_x due to its ability to control the mixing of the fuel with the combustion air. The resulting fuel-rich regions in the primary flame zone are cooled by flame radiation heat transfer prior to completion of combustion with the remaining combustion air. Thus, although the overall air/fuel mixture is near-stoichiometric, the primary NO_x-forming region of the flame is operated at a substoichiometric, low NO_x condition. The NO_x control effectiveness with OSC depends on burner or primary stage stoichiometry which in turn is limited by convective section fouling, unburned hydrocarbon emissions or poor ignition characteristics which occur at excessively rich operation. An additional limitation of fireside corrosion may arise with the firing of some coals and heavy oils.

In off-stoichiometric firing, the flame is long, yellow, and smokey, as opposed to the short and intense flame observed on normal firing. Fuel combustion also extends further into the furnace, sometimes causing excessive superheater (convective section) temperatures. On some units, increased operator vigilance is required to surmount decreased effectiveness of the flame detector system.

In practice, OSC consists of operating some burners (usually the ones located in the lower part of the pattern) fuel-rich while the burners in the upper part of the pattern operate on pure air. Off-stoichiometric combustion is a generic term and several modes of operation are associated with it.

"Two-stage" combustion is based on the same principles as off-stoichiometric combustion except that the fuel-rich burner operation is achieved by diverting a portion of the total required air through separate ports located above the burner pattern. This is also known as "overfire air/NO_x port" operation and is the method used for several new multiburner designs and for use on single burner units such as industrial boilers. Figure 3-6 shows the overfire air system on a corner windbox of a tangentially fired boiler. So-called "simulated overfire air" operation results when the top row of burners operate on pure air. In certain boilers, NO_x reduction optimization requires that the burners operate either fuel- or air-rich in a staggered configuration. This is sometimes called "biased" firing or, in the extreme where some burners are operated on air only, "burners out of service" (BOOS).

The two-stage combustion technique is shown in Figure 3-7. A vertical cross section of a utility boiler burner is shown schematically. Two-stage combustion of natural gas (methane) is depicted, and a few of the global reaction mechanisms associated with the primary and secondary combustion zones are identified.

The effect of two-stage combustion on NO_x emissions from three tangential coal-fired utility boilers is shown in Figures 3-8, 3-9 and 3-10 (Reference 3-31). In these tests, NO_x diminished steadily while first stage air (burner combustion air) was decreased and routed to the overfire air ports. Ninety percent of stoichiometric air supplied to the first stage resulted in a 58 percent NO_x reduction (Figure 3-8). This reduction was obtained with overfire air ports tilted approximately 40 degrees away from the burners (Figure 3-9). NO_x emissions were reduced approximately 40 percent when two-stage combustion with burners out of service was applied on the same boilers (Figure 3-10).

On existing large boilers, a load reduction will result with BOOS firing if the active fuel burners or pulverizers do not have the capacity to carry the fuel required for full load. Most utility boilers constructed after 1971 are, or have been, designed with overfire air ports so that all fuel burners are active during off-stoichiometric operation.

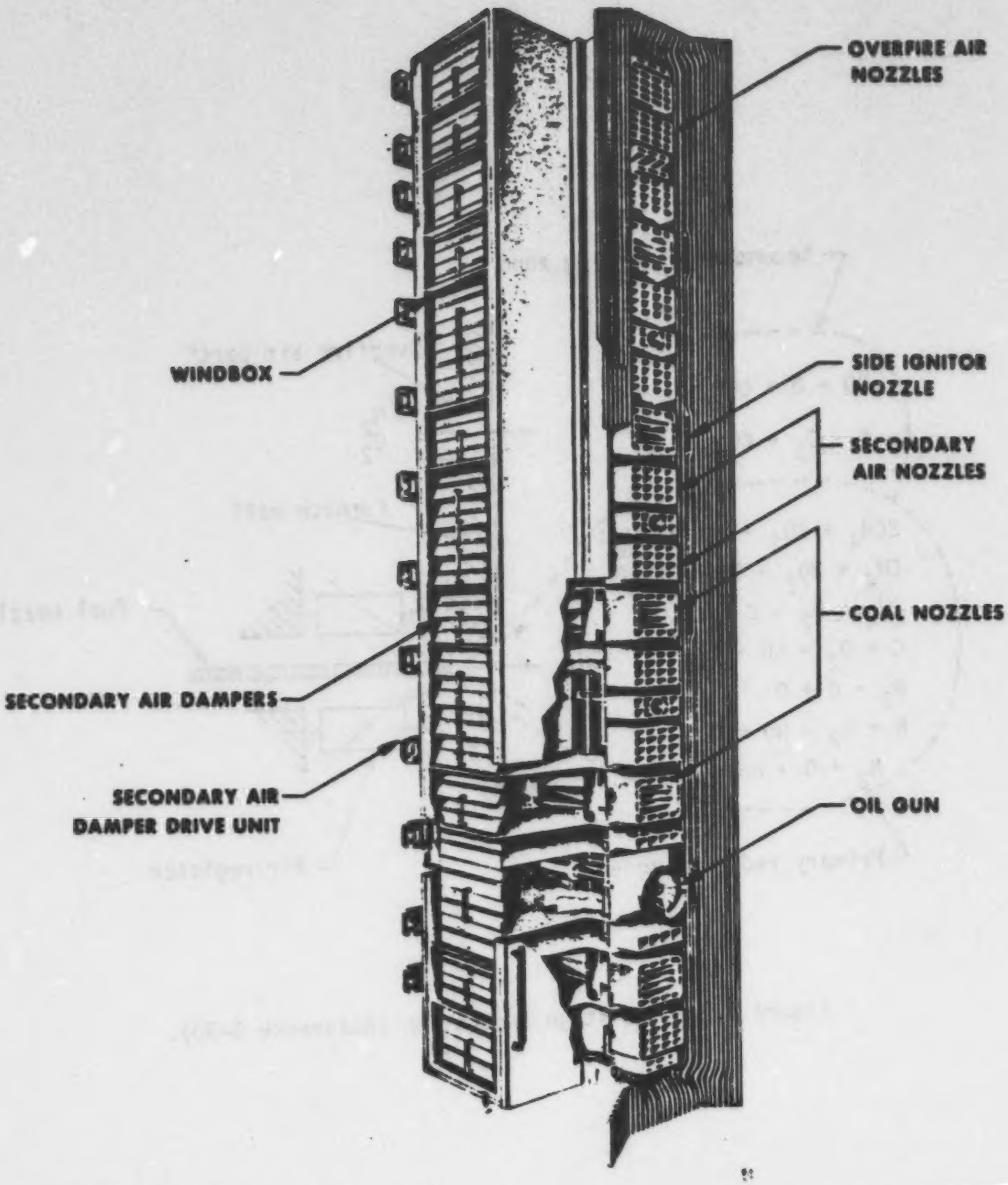

OVERFIRE AIR NOZZLES
WINDBOX
SIDE IGNITOR NOZZLE
SECONDARY AIR NOZZLES
COAL NOZZLES
SECONDARY AIR DAMPERS
SECONDARY AIR DAMPER DRIVE UNIT
OIL GUN

Figure 3-6. Corner windbox showing overfire air system (Reference 3-31).

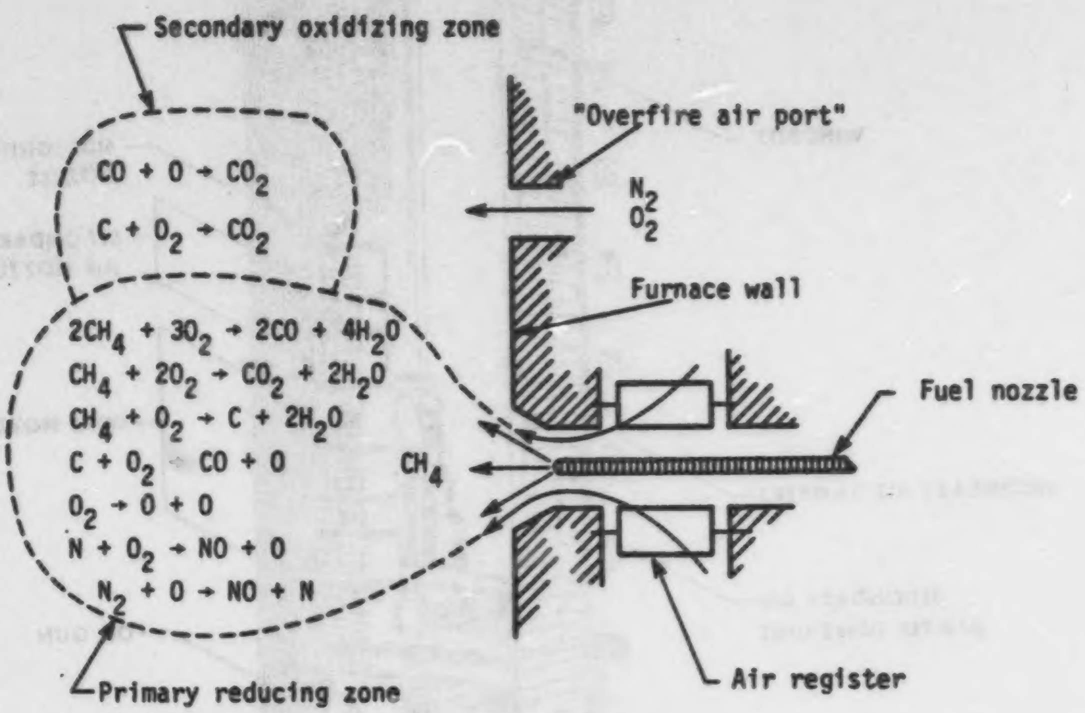

Secondary oxidizing zone
$CO + O \rightarrow CO_2$
$C + O_2 \rightarrow CO_2$
"Overfire air port"
N_2
O_2
Furnace wall
$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
$CH_4 + O_2 \rightarrow C + 2H_2O$
$C + O_2 \rightarrow CO + O$
$O_2 \rightarrow O + O$
$N + O_2 \rightarrow NO + O$
$N_2 + O \rightarrow NO + N$
CH_4
Fuel nozzle
Air register
Primary reducing zone

Figure 3-7. Two-stage combustion (Reference 3-30).

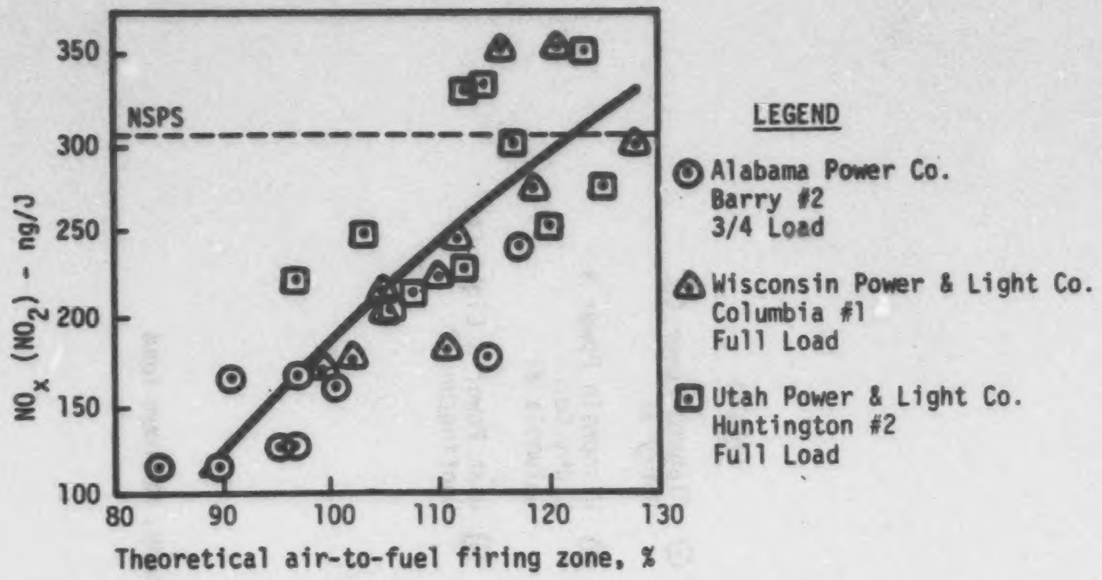


Figure 3-8. NO_x vs. theoretical air, overfire air study (Reference 3-31).

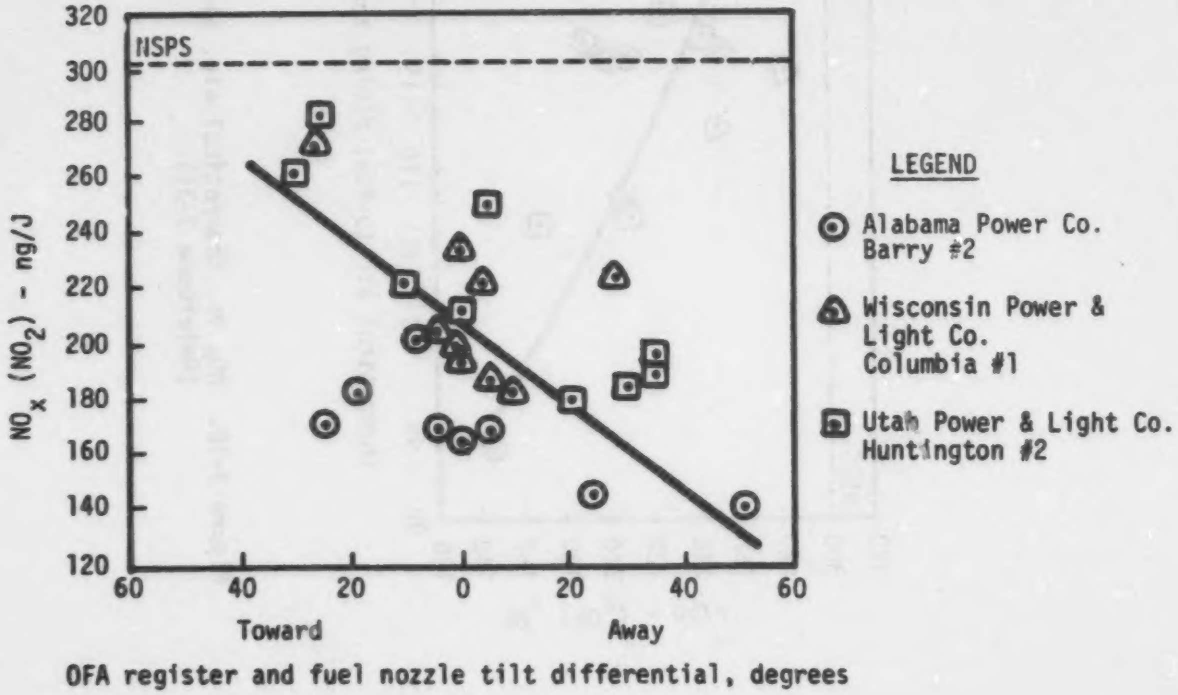


Figure 3-9. NO_x vs. tilt differential, overfire, air study (Reference 3-31).

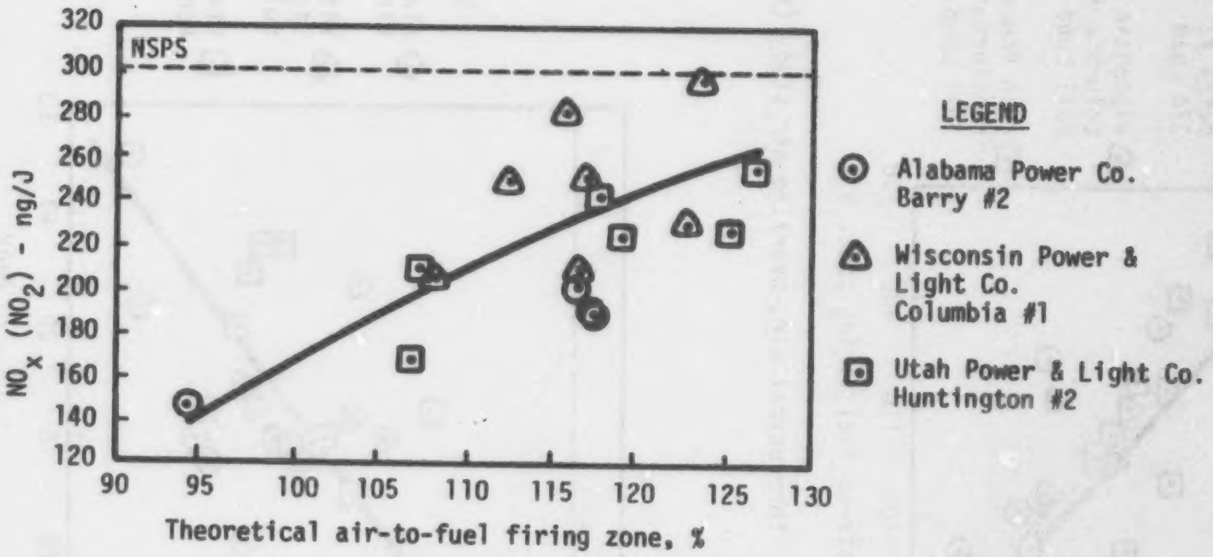


Figure 3-10. NO$_x$ vs. theoretical air, biased firing study, maximum load (Reference 3-31).

With OSC, excess air cannot be generally maintained as low as with normal firing. This is because OSC does not achieve the intimate mixing of fuel and air that is required for low excess air operation.

In early work with OSC, fairly significant results had been obtained for gas-fired utility boilers by Southern California Edison Company and Pacific Gas and Electric Company, and from coal-fired subscale combustion in tests performed by the U.S. Bureau of Mines in 1966. This modification technique has been more thoroughly investigated during the last several years, and subsequent sections of the present document review the recent developments for specific equipment and fuel types.

3.1.2.3 Flue Gas Recirculation

A portion of the flue gas recycled back to the primary combustion zone reduces thermal NO formation by acting as a thermal ballast to dilute the reactants. This reduces both the peak flame temperature and the partial pressure of available oxygen at the burner inlet.

Some large steam boilers are designed for recirculation of a portion of the flue gases in order to control superheat temperatures. Normally, as boiler load decreases, steam temperatures tend to drop unless some method of control is employed. By recirculating an increasing portion of the flue gas as the boiler load decreases, it is possible to maintain steam temperature at a constant level over a wider load range. Where this type of control is used, the flue gases are injected through the hopper bottom to reduce the effectiveness of the furnace heat absorption surface without interfering with the combustion process.

It has been concluded that recirculation for steam temperature control is relatively ineffective in suppressing NO_x. The flue gas must enter directly into the combustion zone if it is to be effective in lowering the flame temperature and reducing NO_x formation.

A typical performance of flue gas recirculation (FGR) is shown in Figure 3-11. These results were obtained on three similar 320 MW tangential, gas-fired utility boilers at full load. The data show a substantial reduction in NO up to 20 percent recirculation and diminishing returns thereafter. Similar results were obtained at reduced load operation (Reference 3-32).

Operational problems are sometimes associated with large rates of FGR. Possible flame instability, loss of heat exchanger efficiency, and, for packaged boilers, condensation on internal heat transfer surfaces, limit the utility of FGR on some units.

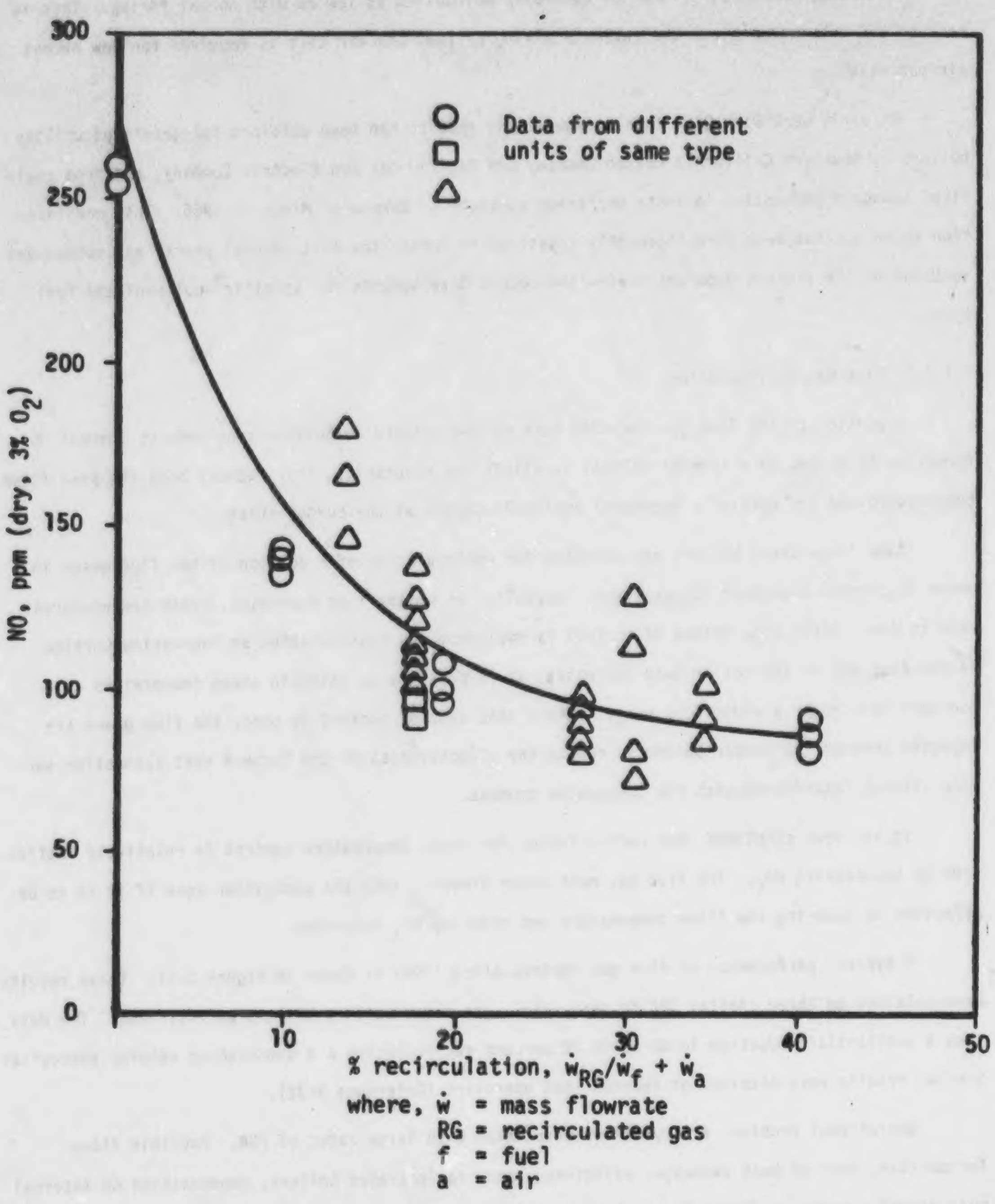


Figure 3-11. Effect of FGR on NO emissions (Reference 3-32).

Although it has been concluded that FGR reduces thermal NO_x, recent experience has cast doubts on its capability to reduce fuel NO_x. This method will, therefore, probably be restricted to low-nitrogen fuels, such as natural gas, distillate oil, and low nitrogen residual oils.

Flue gas recirculation requires greater capital investment than LEA and OSC methods because of the need for high temperature fans and ducts and large space requirements for the modifications. However, for those boilers originally designed with FGR (for superheat control), costs of retrofitting are reasonable (Reference 3-30).

With moderate rates of recirculation (20 percent), FGR can generally be implemented without significantly increasing emissions of CO or HC. At high rates of recirculation (30 percent), however, flame instabilities accompanied by increased CO and HC emissions can result. There is a slight decrease in unit efficiency with FGR due to the recirculation power requirements.

3.1.2.4 Reduced Air Preheat Operation

Reducing the amount of combustion air preheat lowers the primary combustion zone peak temperature, generally lowering thermal NO production as a result. It has been used only sparingly because of the energy penalty. It is applicable to utility steam generators and large industrial boilers which employ heaters to impart about 280K (500F) incremental heat to combustion air. Figure 3-12 shows the NO reduction effect of reduced air preheat temperatures on 320 MW corner-fired boiler burning natural gas. NO emissions were reduced 15 percent at full load with a 45K (80F) reduction in combustion air temperature (Reference 3-32).

With present boiler designs, reducing air preheat would cause significant reductions in thermal efficiency and fuel penalties of up to 14 percent. This technique would be feasible for thermal NO_x control if means other than air preheat were developed to recover heat from 423K to 698K (300F to 800F) gases. Reduced air preheat appears relatively ineffective in suppressing fuel nitrogen conversion (References 3-30, 3-33).

This technique is also applicable to turbocharged internal combustion engines and regenerative gas turbines. The turbocharged IC engines have normally an intercooler to increase inlet manifold air density permitting higher mean flowrates, and consequently higher power output. The reduced air temperature also reduces NO_x emissions.

Regenerative gas turbines recover some of the thermal energy in the exhaust gas (temperatures ranging from 700K (800F) to 867K (110F)) to preheat the combustion air. Any reduction in air preheat causes severe fuel penalties unless other means of recovering the heat in the exhaust can be implemented.

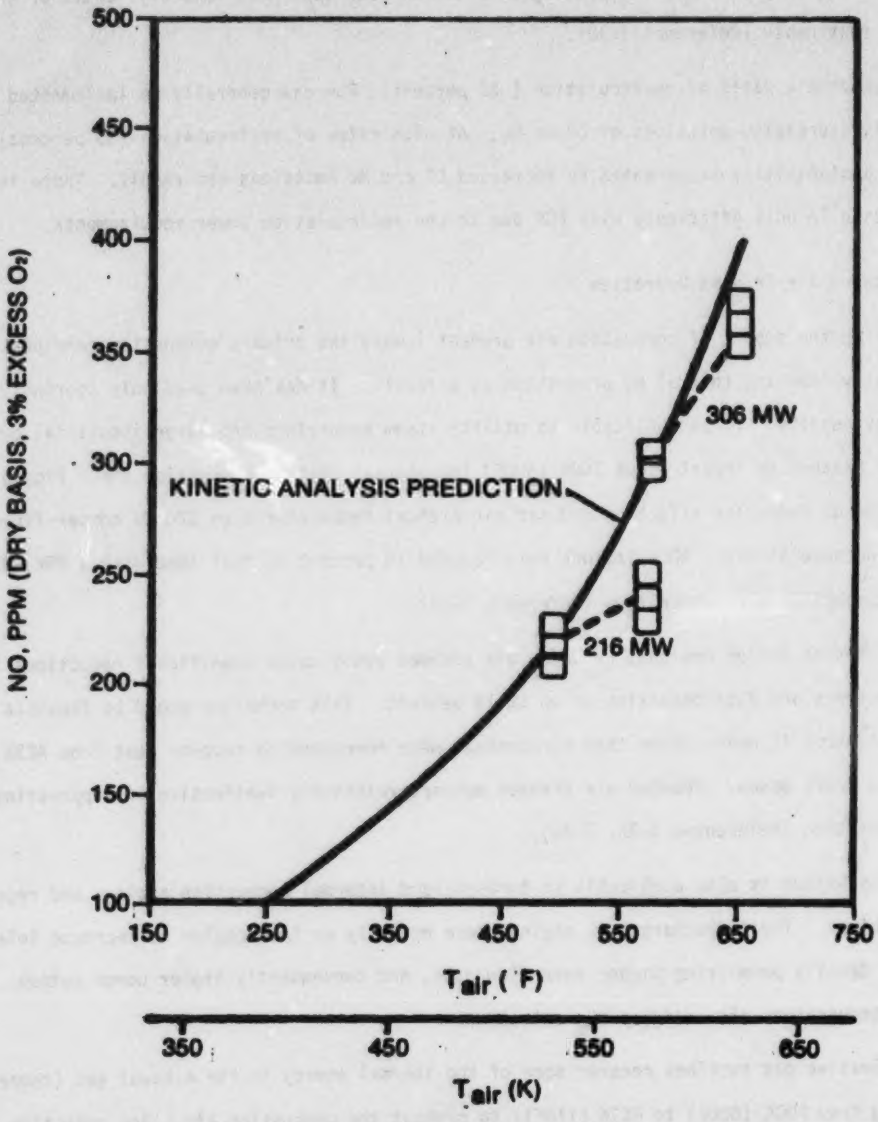


Figure 3-12. Reduced air preheat with natural gas firing, 320 MW corner-fired unit (Reference 3-32).

3.1.2.5 Load Reduction

The term "load" is defined as the percentage of the rated capacity at which the furnace or boiler is being operated. Increasing boiler load causes an increase in primary combustion zone volumetric heat release rate which generally increases the temperature and rate of thermal NO_x formation. Reducing boiler load, or derating, is accomplished by reducing the reactant flow rate (fuel and oxidizer) into the furnace. Both the heat release rate (also known as combustion intensity) and peak flame temperature are lowered.

Apart from the obvious drawback of limiting boiler capacity, load reduction can lead to operational problems. Higher levels of excess air are typically required to suppress CO or smoke emissions thus leading to an overall reduction in efficiency. The increased residence time of the combustion gases at the reduced load can cause steam temperature imbalance in the convective section. Higher excess air or flue gas recirculation may be needed to maintain superheat temperatures. Also, operation at greatly reduced load may exceed the practical turndown limit of the burners. Some burners may need to be taken out of service to maintain good firebox mixing and steam temperature control.

Most of the above problems can be avoided when the unit is designed to operate at low combustion intensity. Here, the use of enlarged fireboxes on new units produces NO_x reductions similar to load reduction on existing units. Some of the last gas- and oil-fired utility boilers sold were equipped with enlarged fireboxes. New coal-fired utility boilers use fireboxes typically 30 percent larger than was the practice in the 1960's (Reference 3-34). This practice is partly in response to the New Source Performance Standards set in 1971 and partly to facilitate combustion of lower grade western coals. With coal-firing, the NO_x reduction due to an enlarged firebox is largely indirect through the change in firebox aerodynamics.

As mentioned in Section 3.1.2.2 the retrofit of off-stoichiometric combustion to achieve significant NO_x reductions often requires derating of the boiler. Derating becomes necessary when the desired first stage burner stoichiometry cannot be obtained with the number of burners out of service (BOOS) at full load conditions. The reduced load, thus, permits additional burners out of service and consequently lowers first stage stoichiometries. Load reduction is therefore also effective in reducing fuel NO_x when this technique is implemented with staged combustion.

3.1.2.6 Steam and Water Injection

Flame temperature, as discussed above, is one of the important parameters affecting the production of thermal NO_x. There are a number of possible ways to decrease flame temperature via thermal means. For instance, steam or water injection, in quantities sufficient to lower flame temperature to the required extent, may offer a control solution. Water injection has been found to be very effective in suppressing NO_x emissions from internal combustion engines and gas turbines. Figure 3-13 shows NO_x emission reductions from a gas turbine as high as 80 percent (Reference 3-35).

Since steam and water injection reduce NO_x by acting as a thermal ballast, it is important that the ballast reach the primary flame zone. Combustion equipment manufacturers vary in their methods of water or steam introduction. The ballast may be injected into the fuel, combustion air, or directly into the combustion chamber.

Water injection may be preferred over steam in many cases, due not only to its availability and lower cost, but also to its potentially greater thermal effect. In gas- or coal-fired boilers, equipped for standby oil firing with steam atomization, the atomizer offers a simple means for injection. Other installations will require special rigging so that a developmental program may be necessary to determine the degree of atomization and mixing with the flame required, the optimum point of injection and the quantities of water or steam necessary to achieve the desired effect.

The use of water injection may entail some undesirable operating conditions, such as decreased thermal efficiency due to the high heat capacity of water compared with that of flue gas or other inert diluents, and increased equipment corrosion. This technique has the greatest operating costs of all combustion modification schemes with a fuel and efficiency penalty typically of about 10 percent for utility boilers and about 1 percent for gas turbines. It is, therefore, an unpopular NO_x reduction technique for all combustion equipment except for stationary gas turbines (References 3-30 and 3-33) which, in addition to the lowest reduction in efficiency, showed no major operational problems or reduced equipment life. Water injection for NO_x reduction does not appear to have a significant effect on stack opacity and emissions of CO and HC.

3.1.2.7 Ammonia Injection

The post-flame decomposition of NO by reducing agents has recently shown promise as a method for augmenting combustion modifications if stringent emission limits are to be met. Exxon has patented a process for the homogeneous gas phase selective decomposition of NO by ammonia (Reference 3-36). The gas phase reaction in the temperature range of 978K (1,300F) to 1,368K

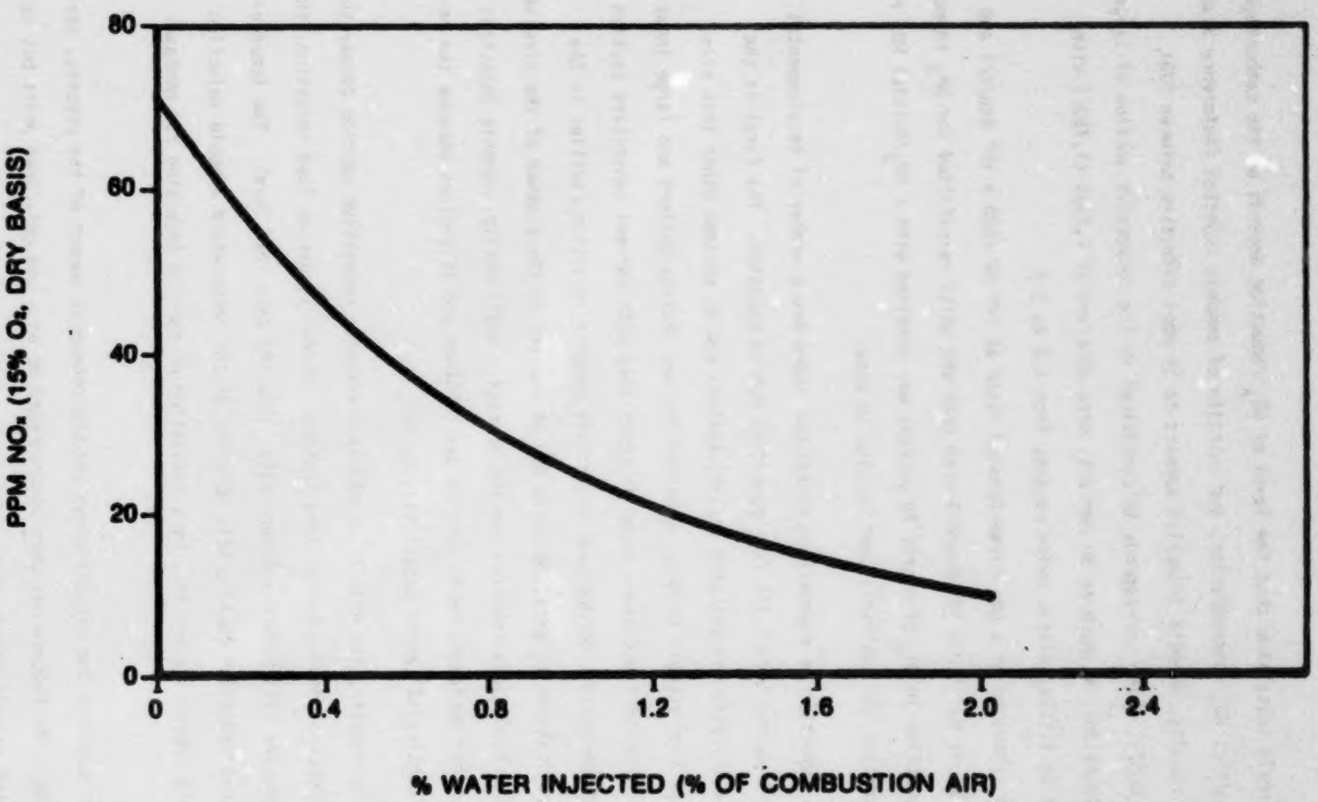


Figure 3-13. Correlation of NO_x emissions with water injection rate for natural gas fired gas turbine (Houston L&P Wharton No. 43 unit) (Reference 3-35).

(2,000F) converts nitric oxide, in the presence of oxygen and ammonia, into nitrogen and water (Reference 3-37).

Results of lab scale tests show that the level of NO_x reduction depends on the combustion product temperature, initial NO_x concentration, and quantity of ammonia injected (Reference 3-38). Based on the available results, ammonia injection appears to be most effective between 978K (1,300F) and 1,368K (2,000F), which corresponds to conditions in the convective section of large boilers. Maximum NO reductions, as much as 90 percent, were obtained at 1,233K (1,750F) with molar ratios of ammonia to initial nitric oxide ranging from 1.0 to 1.5.

Field tests were conducted on a gas-fired furnace rated at 147 MW (500 x 10^6 Btu/hr) and on an oil-fired boiler rated at 41 MW (140 x 10^6 Btu/hr) with both the units retrofitted for NH_3 injection (Reference 3-37). A reduction in NO_x of nearly 70 percent was obtained with a NH_3/initial NO_x ratio of 4.5. Table 3-5 summarizes the available test results to date.

Although ammonia injection is a promising technique, there are a number of developmental questions which must be answered before its full potential can be assessed. The first is the applicability of ammonia injection to existing utility boilers and to systems other than steam generators. Ammonia injection appears to have potential for new utility boilers and large industrial boilers since the required temperature range is compatible with current convective section design. New units could conceivably be designed to include ammonia injection cavities in the convective sections. Applications to existing units may be limited by the absence of the precise residence time-temperature conditions required for the process. Additionally, ammonia injection seems to be limited for other equipment types such as gas turbines and IC engines because the required time-temperature constraint cannot practically be met.

The second question concerns the ability to maintain adequate convective section temperatures required for selective reduction during boiler load changes. Normally, during load reduction, the convective section temperature will reduce substantially below the base load level. The temperature excursions during load reduction could easily move out of the range where ammonia injection is effective. Load following capability may thus be a limitation on ammonia injection for nonbaseloaded units.

The third question concerns the effectiveness and environmental impact of the process, particularly with coal firing. The process has been demonstrated on oil- and gas-fired units but is just starting to be studied in coal-fired pilot scale units. Environmental concerns with ammonia injection include the presence of ammonia as a primary pollutant in the stack gas and potential

TABLE 3-5. SUMMARY OF RESULTS WITH AMMONIA INJECTION (Reference 3-37)

Equipment/ Description	Temperature Range Tested (K)	Range of NH_3 concentration (ppm)	Range of Initial NO_x Concentration (ppm)	Range of Final NO_x (ppm)	Comments/ Remarks
Experimental combustor, 585 kW (2 x 10^6 Btu/hr) firing either gas or oil	920-1,480	0-5,250	100-1,000	10-100	Maximum NO_x reduction occurs at 1,230K, most effective with high initial NO_x concentrations
Experimental tubular reactor	870-1,300	400	250	10-100	Maximum NO_x reduction occurs at 1,250K (without H_2 injection)
	870-1,300	400	250	10-250	Maximum reduction occurs at 980K with H_2 addition
Oil-fired 41 MW (140 x 10^6 Btu/hr)	-	$\frac{NH_3}{NO_{initial}} = 1$ to 4.5	-	30-65% reduction	-
Gas-fired furnace 147 MW (500 x 10^6 Btu/hr)	-	$\frac{NH_3}{NO_{initial}} = 1$ to 4.5	-	30-80% reduction	

reactions of ammonia with the fly ash and sulfur compounds in coal firing. Since low temperature stack gas reactions are important here, pilot scale tests will be of limited use. Full quantification of potential adverse impacts of ammonia injection will await full scale demonstrations with coal firing.

In addition to the above operational concern, there is also the strategic question of whether sufficient ammonia would be available in the 1980's and 1990's for widespread application in utility boilers (Reference 3-39).

In summary, ammonia injection has near-term application for NO_x control in gas- and oil-fired boilers; also, it shows promise for far-term applications to coal-fired boilers.

3.1.2.8 Combinations of Techniques

Since 1969, it has been demonstrated that several of the previously discussed modification techniques can be effectively utilized in combination since they reduce NO_x by different mechanisms. Most often, off stoichiometric combustion is used with low excess air, or load reduction on all fuel-boiler type configurations. For oil and gas fired units flue gas recirculation is used in conjunction with the above techniques. Flue gas recirculation and load reduction lower peak combustion temperatures, while off-stoichiometric operation reduces the amount of fuel burned at peak temperature. For the most part, combining control techniques has been shown to be complementary but not additive for NO_x reduction (Reference 3-30).

3.1.3 Equipment Design Modification

3.1.3.1 Burner Configuration

Burner or combustor modification for NO_x control is applicable to all stationary combustion equipment categories. The specific design and configuration of a burner has an important bearing on the amount of NO_x formed. Certain design types have been found to give greater emissions than others. For example, the spud-type gas burner appears to give a higher emission rate than the radial spud type, which, in turn, produces more NO_x than the ring type.

During the early 1970's specially designed "low-NO_x" burners were produced for thermal NO_x control. For the most part, they are designed for utility and industrial boilers and employ in-flame LEA, OSC, or FGR principles. The aim is to strike a balance between minimum NO_x formation and acceptable combustion of carbon and hydrogen in the fuel.

There are currently several commercial low-NO_x gas and oil burner designs in operation and development (References 3-40 through 3-44). Full scale test results in Japan show reduction in

NO_x emissions from 40 to 60 percent with low-NO_x gas burners. Sub-scale tests with single burners of the type normally used in utility boilers have indicated that simple changes in burner block and nozzle geometry and in swirl vane angles can decrease NO_x production by up to 55 percent (References 3-41 and 3-45). Some of the more innovative methods for oil burners include: flame splitting distributor tips which cause a flower petal flame arrangement, and atomizers with fuel injection holes of different diameters which create fuel-rich and fuel-lean combustion zones (References 3-15, 3-40, 3-43). Up to 55 percent reductions in NO_x emissions are reported with the use of these nozzle tips. However, the change in flame shape may cause problems due to impingement on walls and effectiveness may be reduced as flames interact in multiburner furnaces.

Other air-fuel modifications include a low-NO_x burner (offered by at least one company in the U.S.) for oil- and gas-fired package boilers. This burner uses shaped fuel injection ports and controlled air-fuel mixing to create a thin stubby ring-shaped flame (References 3-40, 3-42). With this modification, reductions in NO_x from 20 to 50 percent are claimed. The most extensive air-fuel modifications involve the self-recirculating and staged combustion chamber type of burners, used in industrial process furnaces. These burners are equipped with a prevaporization or a precombustion chamber in the windbox. In the chamber, the fuel is vaporized and premixed with part of the combustion air, or is allowed to undergo partial combustion under oxygen deficient conditions before being discharged into the furnace. NO_x reductions of about 55 percent are typical for these devices.

Similar reductions are being demonstrated on prototype coal-fired units. One major utility boiler manufacturer has recently fabricated and tested a dual register pulverized coal burner, designed to produce a limited turbulence, controlled diffusion flame. The manufacturer claims NO_x reductions of 50 percent (Reference 3-46). Figure 3-14 shows field test results on three existing boilers equipped with the new low-NO_x burners (Reference 3-47). Emissions were 55 percent less NO_x than identical units operating under similar conditions with old circular burners (Reference 3-26).

The new low-NO_x burners are designed to attain controlled mixing of fuel and air in a pattern that keeps the flame temperature down and dissipates the heat quickly. Burners can be designed to control flame shape for minimizing the reaction at peak temperature between nitrogen and oxygen. Other designs internally recirculate part of the combustion gases or have fuel-rich and fuel-lean regions within a burner to reduce flame temperature and oxygen availability.

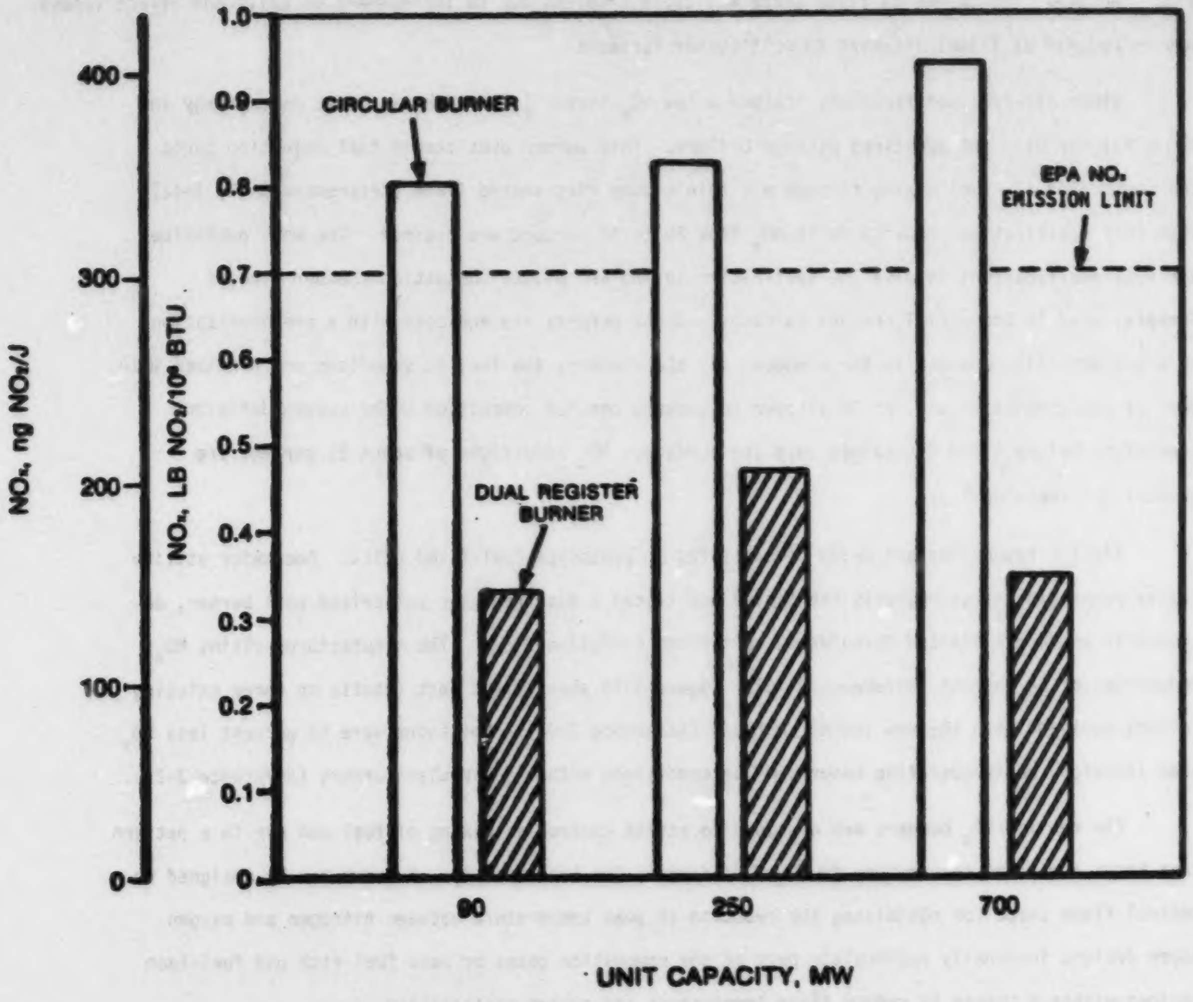


Figure 3-14. Comparison of NO_x emissions with pulverized coal firing, circular burner vs. dual register burner (Reference 3-47).

Burner design modifications have the major advantages of not requiring redesign of boilers or combustion chambers, not necessitating load reduction, and possible applicability to many types of boilers. The disadvantages are that some burners may have to be custom designed for specific fuels and that some burner designs optimized for low-NO_x may only be applicable to a limited number of boiler configurations. However, improved burner design may in the early 1980's be used in conjunction with some already proven external combustion modification such as OSC. This combination of low-NO_x burners and OSC may lead to significantly lower NO_x emissions. It is also possible that with more advanced burner designs currently under development, the external combustion modifications might be entirely replaced with the low-NO_x burners (References 3-33, 3-48).

3.1.3.2 Burner Spacing

The interaction between closely spaced burners, especially in the center of a multiple-burner installation, increases flame temperature at these locations. There is a tendency toward greater NO_x emissions with tighter spacing and a decreased ability to radiate to cooling surfaces. This effect is illustrated by the higher NO_x emissions from larger boilers with greater multiples of burners and tigher spacing. During a field test program conducted by KVB Inc. two 215 MW units were tested for NO_x reduction by combustion modification. These two units are identical in design except for burner spacing. At reduced load operation the closeness of burner spacing for one of the units resulted in higher NO_x levels by as much as 25 percent (Reference 3-32).

In most new utility boiler designs, vertical and horizontal burner spacing has been widened to provide more cooling of the burner zone area. In addition, the furnace enclosures are built to allow sufficient time for complete fuel combustion from slower and more controlled heat release rates, such as that associated with the off-stoichiometric operating mode. Furthermore, furnace plan areas have been increased to allow for larger heat transfer to the cooling walls. This increase in the burner zone dimensions creates more wall area thus increasing the distance between evenly spaced burners.

Horizontal burner spacing is largest for tangentially fired boilers with the burners being located at each corner of the furnace. Flames in a corner-fired unit interact only at the center of the furnace in the well known spiral configuration. As a result the flames radiate widely to the surrounding cooling surfaces before interacting with one another. Also, the tangential firing configuration results in slow mixing of fuel with the combustion air. For these reasons, tangentially-fired boilers show baseline, uncontrolled emissions below those for other utility boilers firing configurations. It has been observed, however, that for many tangentially-fired boilers, the NO_x response to operating modifications has been less impressive than from boilers of other designs, even though the magnitude of the initial, uncontrolled emission level was lower (References 3-27, 3-30).

3.1.4 Fuel Modification

Another alternative for controlling NO_x through process alteration is through modification of the fuel. Three candidate techniques are fuel switching, fuel additives, and fuel denitrification.

3.1.4.1 Fuel Switching

This method usually entails the conversion of the combustion system to the use of a fuel with a reduced nitrogen content (to suppress fuel NO_x) or to one that burns at a lower temperature (to reduce thermal NO_x). Sulfur control is usually a dominant cost incentive for fuel switching. Natural gas firing is an attractive NO_x control strategy because of the absence of fuel NO_x in addition to the flexibility it provides for the implementation of combustion modification techniques. Despite the superior cost-effectiveness of gas-fired NO_x control, the economic considerations in fuel selection are dominated by the current clean fuel shortage. Indeed, the trend is toward the use of coal for electric power generation and larger industrial processes. Fuel switching to natural gas or distillate oil is not a promising option for widespread implementation (Reference 3-49).

Western coals constitute one abundant alternate source of potentially low-NO_x fuels. The direct combustion of western subbituminous coals in large steam generators generally produces lower NO_x emissions than with combustion of eastern bituminous coals. Three mechanisms are responsible for lower NO_x emissions: first, western coals in general contain less bound nitrogen than eastern coals on a unit heating value basis; second, the excess O_2 in a steam generator burning western coal can be maintained at very low levels; and third, the high moisture content of western coal produces lower flame temperatures.

The NO_x emissions for a 59Mg (130,000 lb) steam/hr industrial boiler firing pulverized western coal at baseline conditions were 24 percent lower than for eastern coals (Reference 3-29); NO_x emissions remained unchanged when firing western coal in stokers. However, the slope of the NO_x vs. excess O_2 curve for a water-cooled vibrating grate stoker firing western coal (Wyoming Bighorn) was 12 ppm/percent excess O_2, compared to 35 ppm/percent excess O_2 for eastern coal (Kentucky Vogue).

Some specific problems associated with burning low sulfur, high moisture content coals in combustion equipment designed for higher quality coals are listed below (Reference 3-50):

- Poor ignition
- Reduced boiler load capacity
- Increased carbon loss
- Boiler fouling
- High superheat steam temperature
- Flame instability
- Increased boiler maintenance
- Reduced boiler efficiency
- Reduced collection efficiency of electrostatic precipitator (ESP)

However, most of these operational problems can be solved with current boilers specifically designed to burn these lower grade coals.

Formerly, a major incentive for switching to western coals was the low sulfur content of these fuels. Economic conditions made fuel switching from high sulfur eastern bituminous coals to low sulfur western subbituminous coal competitive with the cost of gas scrubbing for SO_2 removal. Therefore, low sulfur, low nitrogen, western coals represented a promising short-range option in fuel switching for large industrial and utility boilers. However, the 1977 Clean Air Act requires that NSPS be based on a percentage reduction in the pollutant emissions which would have resulted from the use of fuels which are not subject to treatment prior to combustion. This deemphasizes fuel switching.

A promising long-range option is the use of clean synthetic fuels derived from coal. Candidate fuels include low to high Btu gas (3.7 to 30 MJ/Nm^3, or 100 to 800 Btu/scf) and synthetic liquids and solids. Process and economic evaluations of the use of these fuels for power generation are being performed by, among others, the EPA, DOE, the American Gas Association, and the Electric Power Research Institute (EPRI). Two alternatives for utilizing low- and intermediate-Btu gases (up to 26 MJ/m^3, or 700 Btu/scf) are firing in a conventional boiler or in a combined gas and steam turbine power generation cycle. For both systems, economic considerations favor placement of both the gasifier and the power cycles at the coal minehead. The most extensive use of these systems would probably be for replacement of older conventional units upon their retirement (Reference 3-51).

The NO_x emissions from lower-Btu gas-fired units are expected to be low due to reduced flame temperatures corresponding to the lower heating value of the fuel. The effects on NO_x formation of the molecular nitrogen and the intermediate fuel nitrogen compounds, such as ammonia, in the lower-Btu gas have not yet been fully determined and require further study.

The synthetic fuel oils or solid solvent refined coal (SRC) may be expected to be high in fuel nitrogen content even though some denitrification may occur in the desulfurization process. This high nitrogen, carried over from the parent coal, would promote high NO_x emissions. Other potential alternate fuels that might be considered and their potential for fuel or thermal NO_x are listed in Table 3-6.

TABLE 3-6. NO_x FORMATION POTENTIAL OF
SOME ALTERNATE FUELS

FUEL	THERMAL NO_x	FUEL NO_x
Shale oil	Low	High
Coal-oil mixture	Low	Moderate
Methanol	Low	Low
Water-oil emulsion	Low	Unchanged
Hydrogen	High	Low

Shale oil ranks second to coal as the most abundant source of nonpetroleum fossil fuel in the United States (Reference 3-52). Even though there are six proven recovery processes, current shale oil production is very limited. The combustion of shale oil will cause higher levels of fuel NO_x because this fuel generally contains bound nitrogen in excess of 2 percent. Distillation of shale oil would reduce fuel nitrogen content, however.

Coal-oil mixtures have recently become of interest as an alternate fuel which could stretch the domestic oil supplies and reduce our dependence on foreign oil. NO_x from combustion of this fuel will depend on the quantity of nitrogen present in the coal and oil and the percentages of coal and oil used to make the mixture. However, NO_x emissions are expected to be lower than emissions obtained from combustion of coal only.

Methanol is currently produced from the synthesis of methane from natural gas. However, due to the shortage of natural gas, future production will have to come from synthetic gas generated from coal and biomass. Baseline NO_x emissions from the combustion of methanol in an experimental hot wall furnace system were reported at 50 to 70 ppm, compared to 240 to 300 ppm for distillate oil. With flue gas recirculation, the NO_x emissions from methanol combustion were reduced to 10 ppm or 15 percent of the baseline level (Reference 3-53).

In gas turbines 74 percent less NO_x was produced using methanol, compared to distillate oil. The hot wall experimental furnace showed a 20 percent increase in stack heat loss (SHL), compared to SHL of 14 percent for distillate oil (based on 115 percent theoretical air at a 473K (390F) stack temperature). For natural gas, turbine efficiency levels increased by 6 percent due to higher inlet temperatures.

Since water-oil emulsions affect only thermal NO_x these alternate fuels have a definite NO_x reduction potential when distillate oil is used (Reference 3-54). NO_x emission levels from emulsions with approximately 50 mass percent water in distillate oil approached the levels obtained from methanol combustion (Reference 3-55).

Hydrogen as a fuel is used in high energy production concepts such as rocket engines. The high levels of thermal energy released make this fuel attractive for other energy conversion systems. Thermal NO_x levels are, however, high when hydrogen meets with oxygen in the presence of atmospheric nitrogen. Water represents an abundant supply of hydrogen with the use of electrolysis.

Low NO_x application of these fuels may require development of additional control technologies. Many of the current combustion control strategies may, however, be applicable, especially for the case of thermal NO_x.

The feasibility of synthetic fuel firing as a NO_x control option is contingent on the cost tradeoff between synthetic fuel production and the total control costs for NO_x, SO_x, and particulates in conventional coal firing. In the case of coal derived fuels, there is preliminary evidence that gasification may be more costly than flue gas cleaning of conventional systems.

3.1.4.2 Fuel Additives

For purposes of this document, a fuel additive is a substance added to any fuel to inhibit formation of NO_x when the fuel is burned. The additive can be liquid, solid, or gas. For liquid fuels, the additive should preferably be a liquid soluble in all proportions in the fuel, and it should be effective in very small concentrations. The additive should not in itself create an air pollution hazard nor be otherwise deleterious to equipment and surroundings.

In 1971, Martin, et al., tested 206 fuel additives in an oil-fired experimental furnace, and four additives in an oil-fired packaged boiler. None of the additives tested reduced NO emissions but some additives containing nitrogen increased NO formation (Reference 3-56). Fuel additives reduced NO_x emissions from gas turbines by an average of 15 to 30 percent but are not attractive due to added cost, serious operational difficulties and the presence of the additives, as pollutants, in the exhaust gas (Reference 3-57). Average NO_x reductions of 15 to 18 percent have been recorded using fuel additives in diesel engines (Reference 3-58).

In summary, the results of recent studies on fuel additives for NO_x control have been mixed. In some cases additives had a significant effect on NO emissions, while in other studies they did not. Overall, the use of additives for controlling NO_x is not attractive due to added costs, serious operational difficulties and the presence of the additives as pollutants in the exhaust gas. However, it has been proposed that some fuel additives may provide a peripheral benefit to NO_x control, by allowing increased flexibility in applying combustion modification techniques. This concept has yet to be investigated, but could result in lower NO_x emissions.

3.1.4.3 Fuel Denitrification

Fuel denitrification of coal or heavy oils could in principle be used to control the components of NO_x emission due to conversion of fuel bound nitrogen. The most likely use of this concept would be to supplement combustion modifications implemented for thermal NO_x control. Current technology for denitrification is limited to the side benefits of fuel pretreatment to remove other pollutants. There is preliminary data to indicate that marginal reductions in fuel nitrogen result from oil desulfurization (Reference 3-59) and from chemical cleaning or solvent refining of coal for ash and sulfur removal (Reference 3-60). The low denitrification efficiency of these processes does not make them attractive solely on the basis of NO_x control. They may prove cost effective, however, on the basis of total environmental impact.

3.1.5 Alternate Processes

3.1.5.1 Fluidized Bed Combustion

In a fluidized bed combustor (FBC) combustion occurs in an air-supported bed of relatively large (~3.2mm) coal ash and sand or limestone particles. The temperature in the bed is generally in the range of 1,073K to 1,273K (1,500F to 1,900F) which makes the combustion process self-sustaining. The combustor may be at atmospheric pressure (AFBC) or it may be pressurized (PFBC).

A 30 MW AFBC pilot plant began operation in late 1976 (Reference 3-61). Pressurized systems are still being tested, with a pilot plant planned for the early 1980's. Results of recent work in FBC, the status of FBC development, and EPA, ERDA and EPRI FBC programs can be found in Reference 3-61.

Suggested advantages for fluidized bed combustion compared to conventional boilers are: (1) compact size yielding low capital cost, modular construction, factory assembly and low heat transfer area, (2) higher thermal efficiency yielding lower thermal pollution, (3) lower combustion temperature resulting in less fouling and corrosion and reduced NO_x formation, (4) potentially efficient sulfur oxides control by direct contact of coal with an SO_2 acceptor, (5) fuel versatility, (6) applicable to a wide range of low-grade fuels including char from synthetic fuels processes, and (7) adaptable to a high efficiency gas-steam turbine combined power generation cycle. The general validity of these suggested advantages have yet to be demonstrated in field application. The principle disadvantages of FBC are: (1) potential large amounts of solid waste (the sulfur acceptor material) and (2) heavy particulate loading in the flue gas.

The feasibility of the FBC for power generation and utility boilers depends in part on the following: (1) development of efficient methods for regeneration and recycling of the dolomite/limestone materials used for sulfur absorption and removal, (2) obtaining complete combustion through fly ash recycle or an effective carbon burnup cell, (3) development of a hot-gas particulate removal process to permit use of the combustion products in a combined-cycle gas turbine without excessive blade erosion.

Oxides of nitrogen emissions from fluidized bed combustors have been shown to be predominately fuel-derived. Seven to ten percent of fuel nitrogen is converted to NO_x (References 3-62 and 3-63). Experiments with nitrogen-free fuels resulted in NO_x concentrations in agreement with equilibrium values at the bed temperature. However, coal-fired experiments resulted in NO_x concentrations in excess of the equilibrium values. Furthermore, experiments using nitrogen-free gases with coal yield substantially similar NO_x levels as combustion in air (Reference 3-62).

NO_x emissions have been found to be slightly dependent on coal particle size, the type and amount of sulfur acceptor, the amount of excess air and the design of the combustor itself. Emission levels from pressurized fluidized bed combustors are significantly less than from atmospheric combustors. This is probably a result of greatly increased NO_x decomposition rates at elevated pressures. Even at 100 percent excess air, NO_x emissions from a PFBC are well below the current standards of 300 ng NO_2/J (0.7 lb/10^6 Btu). Results of 160 ng/J (0.37 lb/10^6 Btu) have been reported (Reference 3-61).

In general, NO_x control in FBC is a matter of good management of the normal process variables. If more stringent standards are enacted, conventional NO_x controls, such as flue gas recirculation and off-stoichiometric combustion, may be used. Exploratory results indicate that two-stage combustion could be advantageous for both NO_x and SO_x control. The flexibility of the FBC process is a technical and cost advantage to the implementation of new control techniques.

From a NO_x control standpoint, fluidized bed combustion appears to be competitive with control of conventional combustion methods. At the present time, however, FBC must be viewed as a medium risk concept. The economics of the basic process have not yet been fully established relative to conventional boilers or low-Btu gas combined cycle units. Also, the versatility of the FBC concept to a wide variety of equipment applications needs to be shown.

3.1.5.2 Catalytic Combustion

Catalytic combustion refers to combustion occurring in close proximity to a solid surface which has a special (catalytic) coating. A catalyst accelerates the rate of a chemical reaction, so that substantial rates of burning should be achieved at low temperatures, avoiding the formation of NO_x. Moreover, the catalyst itself serves to sustain the overall combustion process, thereby minimizing the stability problems (References 3-64 and 3-65). However, the overall success of a catalytic combustion system in reducing CO and UHC to low levels is a function of both heterogeneous and gas phase reactions; surface reactions alone appear to be unable to achieve the desired low levels.

Emissions from catalytic combustion experiments have typically been: $NO_x < 2$ ppm, UHC = 4 ppm, and CO = 10 to 30 ppm. Both gaseous and distillate fuels have been used and combustion efficiencies above 95 percent have been obtained (Reference 3-65).

The catalyst bed temperature must be held below 1,811K (2,800F) to minimize the formation of NO_x. At high temperatures, above 1,273K (1,830F), catalyst degradation can be significant. Excess air can be used to lower the bed temperature; but except for gas turbines excess air is unattractive since it also reduces thermal efficiency. Further research is underway to consider other systems, such as catalyst bed cooling, exhaust gas recirculation and staged combustion to maintain a low bed temperature.

Recent tests evaluated the applicability of catalytic combustors for gas turbines. Test fuels used were No. 2 distillate oil and low Btu synthetic coal gas, for a range of pressure, temperature, and mass flow conditions. Test results show that the catalyst bed temperature profile at the bed exit was very uniform for low Btu gas, but not as uniform for No. 2 oil. Exceptionally low emissions (2 to 3 ppm NO_x, 20 to 30 ppm CO) were achieved for both fuels, and unburned hydrocarbons (UHC) were less than 1 ppm (Reference 3-66). However, much additional work is needed before catalytic combustion can be applied to gas turbines in the field.

Catalytic combustion has been demonstrated to be effective in removing pollutants such as NO_x, CO, and UHC, but at present, catalytic combustors are limited by the catalyst bed temperature capability. Various government agencies and private industries are developing catalysts that will withstand high temperatures, retain high catalyst activity, and last longer. Catalytic combustion systems are also under development; it appears that during the next 5 to 10 years, catalytic combustion concepts may be incorporated into new gas turbine and residential, commercial, and industrial heating designs.

3.1.5.3 Repowering

Repowering adds a combustion turbine to an existing steam plant, providing additional capacity at lower initial costs and lower energy costs than other spare capacities available to a utility.

Repowering includes: (1) steam turbine repowering, in which gas turbines and new heat recovery boilers are added to an existing steam electric generating plant; (2) boiler repowering in which gas turbines are added to the existing steam generating facilities for power generation, requiring the conversion of existing conventional boilers to heat recovery type boilers; and (3) gas turbine repowering in which a steam generating plant is added to an existing gas turbine plant (References 3-67 and 3-68).

Depending on the system and power needs, repowering of existing facilities offers the following advantages:

- There is no need to acquire and develop a new plant site
- Repowering generally requires smaller increments of investment, saving on fixed charges since major investment on new plants is deferred
- Repowering improves heat rate, which lowers fuel consumption
- The environmental impact is reduced, with improving schedules for environmental and site related approvals
- For boiler and steam turbine repowering, there is no increase in cooling water requirements
- Gas turbines may be operated independently as peaking units, which provides greater plant flexibility

References 3-67 and 3-68 describe in detail the application of repowering to boiler, gas turbine, and steam generating plants; savings in capital and operating costs are anticipated. Repowering of two steam turbine units in the City of Glendale, California increased power output by 75 MW and reduced power cost to the consumer by 8 percent (Reference 3-69). Under contract from the Electric Power Research Institute, Westinghouse Electric Corporation is evaluating repowering conventional steam power plants without replacing the boiler. Earlier pilot scale work for EPRI by KVB Inc. shows a low NO_x potential for repowering. The boiler is fired fuel-rich using approximately 85% of the NO_x bearing gas turbine exhaust as the combustion air. The remaining gas turbine exhaust provides the boiler second stage air which is injected through overfire air ports above the fuel-rich primary stage. Up to 55% of the NO_x in the gas turbine exhaust is chemically reduced by the fuel rich primary stage of the boiler. Also, the use of overfire air reduces the NO_x formed in the boiler by up to 50%. The present use of repowering is very limited. It may see extensive use in the 1980's if significant increases in generating capacity are needed.

3.1.5.4 Combined Cycles

Combined cycles may, in the long term, reduce emissions of sulfur oxide, nitrogen oxide, particulate matter, and waste heat while generating power at efficiencies higher than conventional fossil- and nuclear-fueled steam stations (Reference 3-70).

The combined gas and steam turbine system consists of a gas turbine using a coal-derived fuel, which exhausts into an unfired waste-heat-recovery boiler. At the gas turbine inlet, the most economical large scale steam system would operate at 16.6 MPa (2,400 psig) with 811K (1,000F) throttle steam and 811K reheat temperatures. In this system, roughly 66 percent of the power would be generated by the gas turbine; the remaining 34 percent would be generated by the steam boiler system (Reference 3-71).

Combined cycle efficiency improves significantly as the gas turbine inlet temperature is increased. At turbine inlet temperatures of 1,478K (2,200F), an efficiency improvement of 2 percentage points per 55K (100F) increase in turbine inlet temperature is found.

The current status of combined cycles has been reviewed by Papamarcos (Reference 3-72) who concludes that, before combined cycles are commercialized, efficient fuel conversion processes and high temperature gas turbines that can use coal-derived fuels must be developed. He estimates that these developments will take place in some 15 to 20 years, and current DOE projections concur with his estimate.

3.2 COMBUSTION FLUE GAS TREATMENT

Combustion modification is a demonstrated and effective method for achieving reduction of NO_x from stationary sources. It is, however, somewhat limited both in emission reduction efficiency and range of applicability, particularly for coal-fired sources. Removing the NO_x directly from the flue gas can be used in addition to combustion modification when high removal efficiencies are required.

Flue gas treatment (FGT) processes reduce NO_x emissions from combustion sources either by decomposing NO_x to nitrogen and water or oxygen, or by removing NO_x from the gas stream. Work on these systems in the United States is being funded by EPA, but the major work is being conducted in Japan (References 3-40 and 3-73). At present, FGT is commercially available only for oil and natural gas firing. For SO_2 and particulate laden gas streams, FGT for NO_x removal is still in the developmental stage.

For convenience of discussion, the two FGT process routes can be categorized as dry processes (reduction) and wet processes (oxidation followed by scrubbing). Dry systems are operated at about 644K (700F) and generally employ flue gas additives and catalysts. Wet systems employ a wider variety of chemicals and are operated at 313K to 323K (100F to 120F), the same temperatures scrubbers use to remove SO_2. These processes are described separately below.

3.2.1 Dry Flue Gas Treatment

Dry processes are the most fully developed. They are mainly applicable to flue gas streams free of SO_2 and particulates; that is, gases from the burning of gaseous fuels or distillate oils. Large dry FGT systems have been in operation since 1974 in Japan. Some systems applied to SO_2 and particulate laden gas streams have been piloted successfully and several prototype plants are now being constructed to treat gases from residual oil and coal-fired boilers (References 3-40 and 3-48).

Although there are many theoretical dry process variations (e.g., nonselective reduction, selective reduction using NH_3, and molecular sieves), only selective catalytic reduction using ammonia has achieved notable success in treating combustion flue gases for removal of NO_x. The presence of oxygen in concentrations many times greater than NO_x in the flue gas precludes consideration of nonselective reduction. However, selective reduction of NO_x using ammonia is readily accomplished using any of a number of catalysts.

Each process developer utilizes different catalysts, catalyst supports and bed configurations. Also, differing applications require substantially different catalysts and operating conditions depending upon the SO_2 content and dust loading of the specific flue gas. The inlet NO_x concentrations being treated in Japan range from 150 ppm to 250 ppm with NO_x exit concentrations of 10 ppm to 50 ppm (Reference 3-74).

Compared to the wet process, the dry process is simple, requires less space, generates no troublesome byproducts and requires no tail gas reheating. However, the dry process has yet to prove itself on a dirty gas stream of commercial scale. If the sulfur and particulate laden flue gas is scrubbed to remove SO_2 before FGT, it will have to be reheated from about 311K to 643K (100F to 700F) (Reference 3-74). If the SO_2 is not removed from the flue gas excess ammonia may combine with SO_3/SO_2 and cause a visible plume. This byproduct is also corrosive to mild steel. Large amounts of ammonia may be required which will cause an increased consumption of natural gas currently used to produce the ammonia. Ammonia requirements are proportional to the quantity of NO_x removed. Thus, combustion modifications are likely to be used to reduce NO_x levels as much as possible before treatment in FGT systems.

A selective noble metal catalyst process using ammonia was recently explored on a pilot scale by an EPA contractor. The pilot plant, using natural gas, accumulated about 2000 hours of testing and achieved NO_x reductions of 90 percent with essentially no catalyst degradation. Further tests have been conducted using fuel oil and/or sulfur-containing flue gases. These tests indicate that platinum is not satisfactory for flue gases containing SO_2 (Reference 3-74).

Another study for EPA has been conducted for the technical and economic assessment of various catalytic processes for NO_x control (Reference 3-75). Lab scale tests on simulated flue gas investigated several operating variables and catalysts. The major emphasis was on selective reduction of NO_x with ammonia using nonnoble metal catalyst systems. These parametric studies showed NO_x reductions of 60 to 85 percent at inlet concentrations of 250 to 1000 ppm.

Although selective catalytic reduction has been the most widely used dry process, selective noncatalytic NO_x reduction is under investigation in both the U.S. and Japan. The technique involves the homogeneous decomposition of NO_x by injecting a gaseous reducing agent into the post-flame region. Ammonia is the most common reducing agent, although the two U.S. research firms investigating this concept have considered proprietary agents as well. Injected ammonia is most effective for NO_x reduction when the combustion products are between 1,200K and 1,311K (1,700F and 1,900F). The concept has been demonstrated commercially on a 41 MW (140 x 10^6 Btu/hr) oil-fired boiler and a 147 MW (500 x 10^6 Btu/hr) gas-fired furnace. Reductions of 70 percent were achieved with a 1.5:1 molar ratio of ammonia to NO (Reference 3-37).*

Although selective noncatalytic NO_x reduction holds promise, further tests and process studies are needed before its application in the field. The major requirements are: (1) determination of its applicability to systems other than steam generators, such as gas turbines and combined cycles, (2) identification of reducing agent injection rate requirements for retrofit field applications, (3) evaluation of techniques for maintaining adequate convective section temperatures required for selective reduction during boiler load changes, (4) assessment of possible byproduct emissions, and (5) assessment of the impact on reducing agent markets (References 3-37, 3-39, 3-76).

Another dry FGT process that has been identified as a possible NO_x control technique is molecular sieve adsorption. In general, this is not applicable to the water-containing effluents from combustion sources due to preferential absorption of moisture and resultant loss of active sites. It holds promise primarily for specialized noncombustion applications where NO_x concentrations are high (i.e., nitric acid plants).

In general, the considerable experience in Japan qualifies NO_x flue gas treatment by selective catalytic reduction as commercially available for application to gas- and oil-fired sources in the U.S. from a technical standpoint. There are, however, several factors and questions which must be considered in determining the potential for widespread use of this technology in the U.S. Of particular importance is the applicability of this technology to coal-fired sources. EPA's research and development program is aimed at resolving these questions (Reference 3-74).

3.2.2 Wet Flue Gas Treatment

The chemistry and process steps involved in wet processes are considerably more varied than in dry processes (Reference 3-74). All of those systems which have advanced beyond bench scale involve the use of a strong oxidant such as ozone or chlorine dioxide to convert the relatively inactive NO in the flue gas to NO_2 or N_2O for subsequent absorption. Unfortunately, nearly all wet processes result in a troublesome byproduct which may be little commercial value. Some of these byproducts are nitric acid, potassium nitrate, ammonium sulfate, calcium nitrate, and gypsum.

The required oxidation for wet FGT processes can take place either in the liquid or gas phase. Those processes that utilize liquid phase oxidation require extensive liquid/gas contact in order to absorb the inactive NO. It appears that the size and pressure drop of the NO absorber may be so great as to preclude the use of liquid phase oxidation processes on combustion flue gases where large volumes of gas and low NO_x concentrations are involved.

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*Ammonia injection is discussed in more detail in Section 3.1.2.7.

The use of ozone or chlorine dioxide to oxidize NO in the gas stream prior to the scrubber appears to be the more successful approach. Although the required scrubber is still quite large, substantial removal of NO_x can be obtained in a scrubber designed for SO_2 removal. Unfortunately, chlorine dioxide is expensive and its use introduces the problem of disposing of chloride-containing liquid discharges. In addition, the production of ozone requires expensive equipment and a great deal of electrical energy. For coal-fired flue gas with its higher NO_x concentrations, the oxidant cost is very likely to be prohibitive. Also, where ozone is utilized, additional equipment may be required for removal of excess ozone from the final gas stream.

Although wet NO_x FGT systems may not see widespread use in this country, two deserve additional mention because they are relatively simple extensions of well established flue gas desulfurization (FGD) technology. The Chiyoda 101 FGD process has been modified by the inclusion of an ozone generator for NO oxidation. The absorbed NO_x is removed from the system as a dilute calcium nitrate solution requiring disposal. The process has been designated Chiyoda Thoroughbred 102. This simultaneous SO_x/NO_x process has been piloted in Japan but has not seen commercial service as yet.

Mitsubishi Heavy Industries (MHI) also is developing a wet NO_x FGT process which is a fairly simple extension of their limestone FGD process. In this case, two additional pieces of equipment are required: one for ozone generation and injection into the flue gas, and one for treatment of the tail gas to remove unreacted ozone prior to release to the atmosphere. The MHI process differs from most other wet FGT processes in that the captured nitrogen oxides are reduced to elemental nitrogen by reaction with calcium sulfate in the circulating scrubber liquor. A proprietary catalyst present in the scrubber liquor promotes this reaction. This simultaneous SO_x/NO_x process is presently in the pilot plant state in Japan.

Both the Chiyoda and MHI processes are attractive from the standpoint of having simultaneous SO_x/NO_x control capability and from the developmental standpoint since they involve presently commercial FGD technology. However, the high energy consumption associated with the required production of ozone is likely to render wet simultaneous SO_x/NO_x processes impractical. For example, the oxidation of NO to NO_2 by ozone for a 300 MW power plant is estimated to require 3 to 9 percent of the plant power output (Reference 3-77).

It appears that wet FGT systems cannot compete with dry selective catalytic reduction where simple NO_x control is involved. For coal-fired applications where the dust loading and SO_2

concentrations are high, it is not clear whether dry FGT combined with conventional FGD processes will be cheaper than the wet simultaneous SO_x/NO_x systems such as Chiyoda 102 or MHI. Dry simultaneous SO_x/NO_x systems such as the Shell and the Sumitomo Shipbuilding processes may also prove to be cheaper than the wet simultaneous processes. The Shell process is being commercially applied on a 40 MW* oil-fired boiler in Japan and is being applied in the U.S. on the flue gas streams from a 0.6 MW* coal-fired boiler. The Sumitomo Shipbuilding process will be tested at the prototype level on an oil-fired boiler.

In general, wet processes are less well developed and show higher projected costs than dry FGT processes. Considering their cost and complexity, it is doubtful that wet processes would be receiving any development attention in Japan were it not for the potential for simultaneous SO_x and NO_x removal. For both processes, a number of important questions concerning NO_x FGT costs, secondary effects, material use, reliability, and waste disposal remained to be answered. EPA is proceeding with a coordinated program of experimental work, technology assessment, and engineering studies to answer these questions (References 3-48, 3-74).

3.3 Noncombustion Gas Cleaning

Emissions from noncombustion sources as industrial or chemical processes are small relative to the total emissions from stationary sources (1.7 percent). Nationwide NO_x emissions from nitric acid manufacturing are estimated, for the year 1974, at 127 Gg (140,000 tons) uncontrolled emissions, which is about 1.0 percent of the total stationary source emissions. The Environmental Protection Agency issued standards (under the authority of the Clean Air Act) that new nitric acid plants constructed after December 23, 1971, have a maximum permitted nitrogen oxide effluent of 1.5 kg (measured as NO_2) per Mg of acid (100 percent basis) produced (3 lb/ton). This is equivalent to approximately 210 ppm NO_x. For existing plants the maximum nitrogen oxides permitted has been set at 2.75 kg/Mg (5.5 lb/ton) of acid or approximately 400 ppm NO_x in several states. These standards were established in consideration of the then available technology, which was catalytic reduction of NO_x to N_2 and water using methane or hydrogen.

Several economic factors, discussed in Section 3.3.2.4 have stimulated development of improved processes for tail gas cleaning and improvements in the nitric acid process itself. One of the major considerations is that much of the residual oxides of nitrogen formed in the manufacture of nitric acid can be recovered and converted into nitric acid, thus increasing the plant yield. Also, new plants can be designed to have low NO_x emissions without add-on control equipment.

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*electric output rating.

These designs will be described in Section 3.3.1. Techniques suitable for retrofit abatement for older plants or add-on controls for plants built using old technology include catalytic reduction, extended absorption with and without refrigeration, wet chemical scrubbing, and molecular sieve adsorption. These techniques will be described in Section 3.3.2. The techniques used for other noncombustion sources, such as explosive plants and adipic acid plants, are basically the same as those used for nitric acid plants, but vary with choice depending on economies of scale and throughput.

3.3.1 Plant Design for NO_x Pollution Abatement at New Nitric Acid Plants

Nitric acid is manufactured in the United States by the catalytic oxidation of ammonia over a platinum or palladium catalyst with the subsequent absorption of the product gases, primarily NO_2 and NO, by water to make nitric acid. A more detailed discussion of the chemical process is given in Section 6. Each of these two catalytic processes have optimum conversions at different operating conditions. Moderate pressures of 300 to 500 kPa allow longer catalyst life by lowering operating temperatures in the initial oxidation reaction. Higher pressures in the range of 800 to 1100 kPa (116 to 160 psia) allow higher absorption rates in the absorption columns with smaller equipment sizes and lower costs. The higher conversions of NO_2 to HNO_3 allow for smaller equipment for both the main process plus any tail gas treatment required to meet emission standards. Currently most existing plants operate at low or moderate pressures throughout the process. Sections 3.3.1.1 and 3.3.1.2 will discuss how the design of new nitric acid plants has taken these factors into account to increase conversion and decrease emission control costs.

3.3.1.1 Absorption Column Pressure Control

By designing a new plant so that the inlet pressure at the absorption is 800 to 1000 kPa (116 to 145 psia), the efficiency of the absorber can be increased so that an effluent of less than 200 ppm NO_x is emitted. A high inlet gas pressure at the absorber can be achieved either by running the ammonia-oxygen reaction at high pressure, or by running the ammonia-oxygen reaction at low pressure, with compression of the gas stream before introduction to the absorber. Higher absorption pressures will increase the convertion of NO_2 to nitric acid and minimize NO_x emissions. However, there are economic penalties in the form of increased equipment cost, thicker walls and compressors, and increased maintenance costs.

3.3.1.2 Strong Acid Processes

Nitric acid is usually produced at strengths of 50 to 65 percent by weight in water due to azeotrope limitations. Azeotropic conditions result in a constant composition in both vapor and liquid phases. With higher operating pressures nitric acid up to 68 percent can be obtained. Further concentration is sometimes accomplished by dehydration of the acid or further distillation with sulfuric acid addition.

However, nitric acid of high strength can be made directly from ammonia by the Direct Nitric Acid (DSNA) process. Ammonia is burned with air near atmospheric pressure, and the nitrogen oxides are oxidized to nitrogen dioxide in a contact tower. The nitrogen dioxide is then separated from the gas stream by physical absorption in chilled high-concentrated nitric acid, stripped by distillation and then liquified as N_2O_4.

The liquid dinitrogen tetroxide is pumped to a reactor together with aqueous nitric acid. Pure oxygen is added and the dinitrogen tetroxide reacts at a pressure of approximately 5200 kPa (756 psig) directly to highly concentrated nitric acid. Variations on the process can produce both strong (98 to 99 percent) nitric acid and weak (50 to 70 percent) nitric acid at the same plant (Reference 3-78). Tail gas emissions from this process are within the 1.5 g/kg (3 lb/ton) NO_x regulation. This occurs primarily by ensuring oxidation to NO_2 and physical absorption with the concentrated nitric acid at low temperature.

Concentrated nitric acid has also been made by the SABAR (Strong Acid By Azeotropic Reactivication) process. Ammonia combustion occurs at near atmospheric pressure and at 1,123K (1,560F) with the usual waste-heat boiler, tail gas preheater, cooler/condenser effluent train. By mixing the combustion gases with feed air and recycled nitrogen dioxide and compression nearly all the NO is converted to NO_2. Chemical absorption with an azeotropic mixture of about 68 percent (by weight) nitric acid produces a superazeotropic mixture. A 99 percent (by weight) overhead product is produced by vacuum distillation.

3.3.2 Retrofit Design for NO_x Pollution Abatement at New or Existing Nitric Acid Plants

Most existing nitric acid plants were not designed with the present NO_x emission standards in mind. Abatement methods for these plants are installed on a retrofit basis. The available abatement methods include chilled absorption, extended absorption, wet scrubbing, catalytic reduction, and molecular sieve adsorption. In this section, these various control techniques for NO_x are described. These same procedures are also used on new nitric acid plants using the earlier low or moderate operation pressure design where the abatement facility is designed to process the tail gas to meet the 1.5 g NO_2/kg of acid product (3 lb/ton) emission standard.

3.3.2.1 Chilled Absorption

The basic principle involved is that the amount of NO_x that can be removed from the process gas by the absorber (water) increases as the water temperature decreases. Therefore, this method of retrofit provides for chilling of the water prior to entry into the absorption tower or by direct cooling of the absorption trays. This method of NO_x reduction has only provided marginal results and has had problems in continuously meeting the NSPS, especially in warm weather. Refrigeration requirements can prove costly, both in equipment and energy use.

3.3.2.2 Extended Absorption

One of the most commonly used retrofit processes, which has been used effectively to meet the NSPS, is extended absorption. Figure 3-15 shows the flow diagram of a nitric acid plant after addition of the extended absorption system, which consists of an additional absorber and a pump. This method is offered by several licensors both with and without other features such as compression of the tail gas before entry to the additional tower or a supply of chilled water to the absorption column trays. Because of the additional pressure loss in the second column an inlet pressure of at least 700 kPa (101 psia) is preferred to make the economics of this method attractive.

3.3.2.3 Wet Chemical Scrubbing

Wet chemical scrubbing removes NO_x from nitric acid plant tail gases by chemical reaction. Liquids such as alkali hydroxide solutions, ammonia, urea, and potassium permanganate convert NO_2 to nitrates and/or nitrites. These techniques produce a liquid effluent which needs disposal. For three recent techniques — urea scrubbing, ammonia scrubbing and nitric acid scrubbing — the effluent is a valuable byproduct which can be reclaimed and sold as fertilizer.

Caustic Scrubbing

In this process, NO_x in the tail gas reacts with sodium hydroxide, sodium carbonate, or ammonium hydroxide to form nitrite and nitrate salts. Although caustic scrubbing removes NO_x from the tail gas, it has not found extensive use in the industry because of the difficulties encountered in disposing of the spent solution. The alkali metal nitrite and nitrate salts contained in the spent solution become a serious water pollutant if released as a liquid effluent, and their concentrations are too dilute for economic recovery.

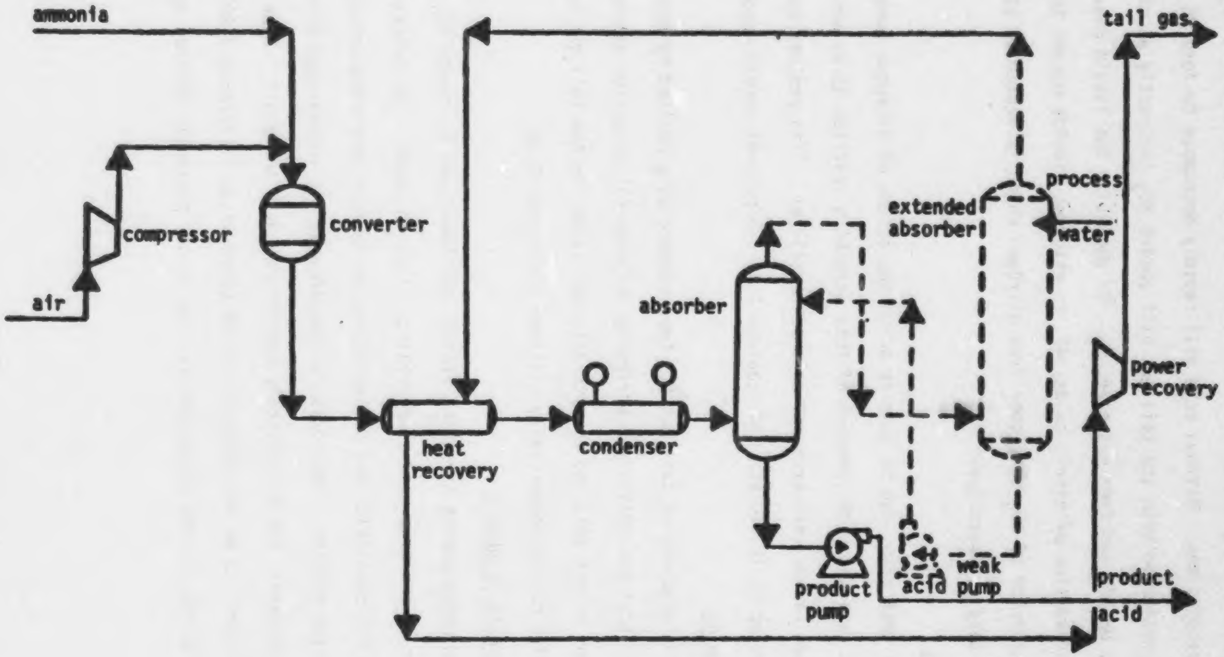
ammonia
air
compressor
converter
heat recovery
condenser
absorber
extended absorber
process water
tail gas
power recovery
product pump
weak acid pump
product acid

Figure 3-15. Extended absorption system on existing nitric acid plant.

Urea Scrubbing

Urea can be used to treat tail gases for NO_x control since it reacts rapidly with nitrous acid. Nitrogen dioxide, NO_2 reacts with water to form both nitric acid (HNO_3) and nitrous acid (HNO_2) in equal proportions. Nitrous acid will rapidly decompose to form NO and NO_2. Urea ($CO(NH_2)_2$) when contacted with the tail gas will absorb NO_2 indirectly as nitrous acid to form ammonium nitrate, NH_4NO_3 and free nitrogen, N_2. By depleting the liquid phase of nitrous acid the equilibrium conversion of nitric oxide, NO, to nitorgen dioxide occurs to remove NO also. The result is conversion of NO_2 to either free nitrogen which is vented to atmosphere or ammonium nitrate which is sold as fertilizer.

Ammonia Scrubbing

Ammonia, a weak base, can be used to scrub the oxides of nitrogen (weak acids) from the nitric acid plant tail gas. The product of this scrubbing reaction is an ammonium nitrate solution (NH_4NO_3) which can be recovered and sold as fertilizer. This process can be applied to tail gas concentrations up to 10,000 ppm and requires 1 to 1.5 percent excess oxygen.

Nitric Acid Scrubbing

Nitric acid scrubbing of tail gas has been commercially applied by one licensor. The process uses both physical absorption and stripping and chemical oxidation absorption. The process uses only water and nitric acid and coverts nitrogen oxides in the tail gas to nitric acid at concentrations which can be commercially utilized (Reference 3-79).

Potassium Permanganate Scrubbing

A potassium permanganate scrubbing process has been used to reduce NO_x emissions from 1800 ppm to 49 ppm at a nitric acid concentration plant in Japan. The process reacts potassium permanganate with nitrogen oxide and sodium hydroxide to form potassium sodium manganate, sodium nitrite and potassium nitrite. The potassium permanganate is regenerated by oxidizing the potassium sodium manganate electrolytically (References 3-80 and 3-81). However, the process is presently considered to be too expensive to be competitive (Reference 3-82). It has not been tried on any plants in the United States, and is not presently offered by any licensor.

3.3.2.4 Catalytic Reduction

There are three types of catalytic reduction processes used for NO_x control: nonselective reduction, which removes both NO_x and oxygen; selective reduction, which removes only NO_x, and heterogeneous catalysis used in conjection with wet scrubbing. Each of these will be discussed in the following paragraphs.

Nonselective catalytic reduction

The nonselective reduction process reacts NO_x with H_2 or CH_4 to yield N_2, CO_2 and H_2O. The process is called nonselective because the reactants first deplete all the oxygen present in the tail gas, and then remove the NO_x. Prior to the large increases in natural gas prices the excess fuel required to reduce the oxygen did not impose a heavy economic penalty. The reactions were exothermic, and much of the heat could be recovered with a waste heat boiler.

The nonselective reduction process is used for decolorization and energy recovery, as well as for NO_x abatement. Decolorization and power recovery units reduce NO_2 to NO and react part of the oxygen, but their capacity to reduce NO to elemental nitrogen is limited. The nonselective abatement units carry the process through to NO reduction as well. In nonselective reduction, the tail gases from the absorber are heated to the necessary catalyst ignition temperature, mixed with a reducing agent, such as hydrogen or natural gas, and passed into the reactor and through the catalyst. The main chemical reactions that take place are:

$$CH_4 + 4NO_2 \rightarrow 4NO + CO_2 + 2H_2O \qquad (3\text{-}6)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (3\text{-}7)$$

$$CH_4 + 4NO \rightarrow 2N_2 + CO_2 + 2H_2O \qquad (3\text{-}8)$$

Similar equations can be written substituting hydrogen for methane, in which case two moles of hydrogen are needed to replace one mole of methane. The reaction kinetics are such that reduction reaction (3-6) is faster than reduction reaction (3-7), but abatement reaction (3-8) is much slower than reaction (3-7). Thus, decolorization can be accomplished by adding just enough fuel for partial oxygen burnout. If NO_x abatement is required, however, sufficient fuel must be added for complete oxygen burnout.

Both catalyst and nitric acid manufacturers report satisfactory performance for decolorization units. The reduction of total NO_x is limited, but ground-level NO_2 concentration in critical areas near the plant is reduced substantially.

NO_x abatement using nonselective catalyst is more difficult technically than decolorization, and commercial results have been less satisfactory. Provisions must be made to control the heat released in reacting all the tailgas oxygen. The thermal control must be done before extensive NO reduction proceeds.

In Section 6 the success of the various types of catalytic abaters in coping with the problems of temperature rise and high space velocities will be discussed. In general, nonselective catalytic reduction is not likely to be used in the future for NO_x control. The availability and cost of natural gas, increasing catalyst cost and poor performance have led to a decline in interest in this process.

Selective catalytic reduction

In selective catalytic reduction, ammonia is reacted with the NO_x to form N_2. The oxygen in the tail gas does not react with the ammonia, so stoichiometric amounts of ammonia are used.

In contrast to nonselective techniques, selective catalyst abatement must be carried out within the narrow temperature range of 483K to 544K (410F to 520F). Within these limits, ammonia will reduce NO_2 and NO to molecular nitrogen, without simultaneously reacting with oxygen. The overall reactions are shown in the following equations:

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12\ H_2O \qquad (3\text{-}9)$$

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \qquad (3\text{-}10)$$

Above 544K, ammonia may oxidize to form NO_x; below 483K, it may form ammonia nitrate.

Selective oxidation with ammonia has several advantages over nonselective reduction:

- The reducing agent, ammonia is usually readily available since it is consumed as feed stock in the nitric acid process
- Temperature rise through the reactor bed is only 20K to 30K (36F to 54F) so that energy recovery equipment, such as a waste heat boiler or high temperature gas turbine, is not required
- Lower raw material costs since the amount of ammonia required is approximately equal to the molal equivalent amount of NO_x abated

Heterogeneous Catalysis

One wet scrubber process uses heterogeneous catalysis in a packed column to oxidize NO to NO_2 (References 3-83 and 3-84). This system is currently in the development stage.

3.3.2.5 Molecular Sieve Adsorption

One method of NO_x control involves the adsorption of NO_x onto a solid followed by regeneration of the adsorbent. Materials such as silica gel, alumina, charcoal, and commercial zeolites or molecular sieves have been employed for this method. Molecular sieves have been found to be the most effective medium for this method of control, since they adsorb NO_2 selectively. Special sieves have been developed which incorporate a catalyst to simultaneously convert NO to NO_2. This process operates best only when low concentrations of oxygen are present, which is true of most tail gas streams. The abatement bed is usually provided with a dehydration section prior to contact with the abatement sieve to improve overall performance.

The adsorbent bed is regenerated by thermally cycling the bed after it is loaded with NO_2. The required regenerating gas is obtained by using a portion of the treated tail gas stream to desorb the adsorbed NO_2 from the bed. This gas stream is then recycled to the nitric acid plant absorption tower. No other liquid, solid or gaseous effluents are produced by this process.

Two plants using this system were in operation and had experienced difficulties. The process has become unattractive for future installations because of the cost of the catalyst bed, the energy cost of thermal cycling, and the operational difficulties of using a cycling adsorption process with a steady state nitric acid plant.

REFERENCES FOR SECTION 3

3-1 Zeldovich, J., "The Oxidation of Nitrogen in Combustion and Explosions," Acta Physiochim, U.S.S.R. (Moscow), 21, 4, 1946.

3-2 MacKinnon, D. J., "Nitric Oxide Formation at High Temperature," Journal of the Air Pollution Control Association, Vol. 24, No. 3, March 1974.

3-3 Rawdon, A. H., and R. S. Sadowski, "An Experimental Correlation of Oxides of Nitrogen Emissions from Power Boilers Based on Field Data," Trans. ASME Journal of Engineering for Power, 95, 3, July 1973.

3-4 Breen, B. P., "Control of the Nitric Oxide Emissions from Fossil Fueled Boilers," The Fourth Westinghouse International School for Environmental Management, July 15-18, 1973.

3-5 Bartz, D. R., et al., "Control of Oxides of Nitrogen from Stationary Sources in the South Coast Air Basin," California Air Resources Board Report No. ARB 2-1471, September, 1974.

3-6 Heap, M. P., et al., "Burner Criteria for NO_x Control, Volume I. Influence of Burner Variables on NO_x in Pulverized Coal Flames," EPA 600/2-76-061a, March 1976.

3-7 Bowman, C. T., et al., "Effects of Interaction Between Fluid Dynamics on Chemistry of Pollutant Formation in Combustion," in Proceedings of the Stationary Source Combustion Symposium, Volume I, Fundamental Research, EPA 600/2-76-152a, June 1976.

3-8 Shaw, J. T., and A. C. Thomas, "Oxides of Nitrogen in Relation to the Combustion of Coal," presented at the Seventh International Conference on Coal Science, Prague, June, 1968.

3-9 Pershing, D. W., et al., "Influence of Design Variables on the Production of Thermal and Fuel NO from Residual Oil and Coal Combustion," AIChE Symposium Series, No. 148, Vol. 71, 1975, pp. 19-29.

3-10 Sarofim, A. F., et al., "Mechanisms and Kinetics of NO_x Formation: Recent Developments," presented at 65th Annual AIChE Meeting, Chicago, November 1976.

3-11 Snyder, R., "Nitrogen and Oxygen Compound Types in Petroleum," Analytical Chemicstry 41: 314-323, February 1969.

3-12 Martin, G. B., and E. E. Berkau, "An Investigation of the Conversion of Various Fuel Nitrogen Compounds to Nitrogen Oxides in Oil Combustion," presented at AIChE meeting, August 30, 1971, Atlantic City, August, 1971.

3-13 United States Senate, Committee on Public Works, "Air Quality and Stationary Source Emission Control," Serial No. 94-4, March 1975.

3-14 Habelt, W. W. and B. M. Howell, "Control of NO Formation in Tangentially Coal-Fired Steam Generators," in Proceedings of the NO_x Control Technology Seminar, EPRI SR-39, February 1976.

3-15 Heap, M. P., et al., "The Optimization of Burner Design Parameters to Control NO_x Formation in Pulverized Coal and Heavy Oil Flames," in Proceedings of the Stationary Source Combustion Symposium, EPA-600/2-76-152b, June, 1976.

3-16 Pohl, J. H., and A. F. Sarofim, "Devolatilization and Oxidation of Coal Nitrogen," presented at 16th International Symposium on Combustion, M.I.T., August 1976.

3-17 Blair, D. W., et al., "Devolatilization and Pyrolysis of Fuel Nitrogen from Single Coal Particle Combustion," 16th Symposium (International) on Combustion, Cambridge, Mass., 1976.

3-18 Pershing, D. W., "Nitrogen Oxide Formation in Pulverized Coal Flames," PhD Dissertation, University of Arizona, 1976.

3-19 Axworthy, A. E., Jr., "Chemistry and Kinetics of Fuel Nitrogen Conversion to Nitric Oxide," AIChE Symposium Series, No. 148, Vol. 71, 1975, pp. 43-50.

3-20 Axworthy, A. E., et al., "Chemical Reactions in the Conversion of Fuel Nitrogen to NO_x," in Proceedings of the Stationary Source Combustion Symposium, Volume I, Fundamental Research, June 1976.

3-21 Pershing, D. W., and J. O. L. Wendt, "The Effect of Coal Combustion on Thermal and Fuel NO_x Production from Pulverized Coal Combustion," presented at Central States Section, The Combustion Institute, Columbus, Ohio, April 1976.

3-22 Pohl, J. H. and A. F. Sarofim, "Fate of Coal Nitrogen During Pyrolysis and Oxidation," In: Proceedings of the Stationary Source Combustion Symposium, Volume I, Fundamental Research, EPA 600/2-76-152a, June 1976.

3-23 Barr, W. H., and D. E. James, "Nitric Oxide Control — A Program of Significant Accomplishments," ASME 72-WA/Pwr-13.

3-24 Barr, W. H., et al., "Retrofit of Large Utility Boilers for Nitric Oxide Emissions Reduction — Experience and Status Report."

3-25 Crawford, A. R., et al., "Field Testing: Application of Combustion Modifications to Control NO_x Emissions from Utility Boilers," Exxon Research and Engineering Co., EPA-650/2-74-066, June 1974.

3-26 Crawford, A. R., et al., "The Effect of Combustion Modification on Pollutants and Equipment Performance of Power Generation Equipment," Exxon Research and Engineering Co., EPA-600/2-76-152c, prepared for the Stationary Source Combustion Symposium, September 24-26, 1975.

3-27 Blakeslee, C. E., and H. E. Burbach, "Controlling NO_x Emissions from Steam Generators," C.E. Inc., APCA 72-75, 65th Annual Meeting of Air Pollution Control Association, June 18-22, 1972.

3-28 Hollinden, G. A., et al., "Evaluation of the Effects of Combustion Modifications in Controlling NO_x Emissions at TVA's Widow's Creek Steam Plant," EPRI SR-39, February 1976.

3-29 Maloney, K. L., "Western Coal Use in Industrial Boilers," Western States Section/The Combustion Institute, April 19-20, 1976, Salt Lake City, Utah.

3-30 Brown, R. A., H. B. Mason, and R. J. Schreiber, "Systems Analysis Requirements for Nitrogen Oxide Control of Stationary Sources," Environmental Protection Technology Series EPA-650/2-74-091, Sepgember 1974.

3-31 Selker, A. P., and R. L. Burnington, "Overfire Air Technology for Tangentially Fired Utility Boilers Burning Western U.S. Coals," in Proceedings of the Second Stationary Source Combustion Symposium Vol II, Utility and Large Industrial Boilers, EPA-600/7-77-073b, July 1977.

3-32 Bagwell, F. A., et al., "Utility Boiler Operating Modes for Reduced Nitric Oxide Emissions," Presented at the 64th Annual Meeting of the Air Pollution Control Association, June 1971.

3-33 U.S. Environmental Protection Agency, "Draft — NO_x SIP Preparation Manual Volume II — Support Sections," Office of Air Quality Planning and Standards, Research Triangle Park, N.C., April, 1976.

3-34 Copeland, J. O., "Standards Support and Environmental Impact Statement: An Investigation of the Best Systems of Emission Reduction for Nitrogen Oxides from Large Coal-Fired Steam Generators," (Draft) EPA, October 1976.

3-35 Crawford, A. R., E. H. Manny and W. Bartok, "Field Testing: Application of Combustion Modifications to Power Generating Combustion Sources," in Proceedings of the Second Stationary Source Combustion Symposium, Volume II, Utility and Large Industrial Boilers, EPA-600/7-77-073b.

3-36 Lyon, R. L., "Method for the Reduction of the Concentration of NO in Combustion Effluents Using Ammonia," U. S. Patent No. 3,900,554, assigned to Exxon Research and Engineering Company, Linden, New Jersey, August 1975.

3-37 Lyon, R. K. and J. P. Longwell, "Selective, Non-Catalytic Reduction of NO_x by NH_3," Proceedings of the NO_x Control Technology Seminar, EPRI SR-39, February 1976.

3-38 Muzio, L. J., and T. K. Arand, "Homogeneous Gas Phase Decomposition of Oxides of Nitrogen," EPRI Report FP-253, August 1976.

3-39 Teixeira, D. P., "Status of Utility Application of Homogeneous NO_x Reduction," Proceedings of the NO_x Control Technology Seminar, EPRI SR-39, February 1976.

3-40 Ando, J. and T. Heiichiro, "NO_x Abatement for Stationary Sources in Japan," Environmental Protection Technology Series, EPA-600/2-76-013b, January 1976.

3-41 Shoffstall, D. R., "Burner Design Criteria for Control of Pollutant Emissions from Natural Gas Flames," Institute of Gas Technology, EPA-600/2-76-152b, June 1976.

3-42 Koppang, R. R., "A Status Report on the Commercialization and Recent Development History of the TRW Low NO_x Burner," TRW Energy Systems Group.

3-43 Tsuji, S., et al., "Control Technique for Nitric Oxide — Development of New Combustion Methods," IHI Engineering Review, Vol. 6, No. 2.

3-44 Ando, J., et al., "NO_x Abatement for Stationary Sources in Japan," August 1976 (Preliminary Draft).

3-45 Shoffstall, D. R., "Burner Design Criteria for Control of NO_x from Natural Gas Combustion, Volume I," Institute of Gas Technology, EPA-600/2-76-098a, April 1976.

3-46 Brackett, C. E., and J. A. Barsin, "The Dual Register Pulverized Coal Burner — a NO_x Control Device," EPRI SR-39, February 1976.

3-47 Campobenedetto, E. J., "The Dual Register Pulverized Coal Burner — Field Test Results," presented at Engineering Foundation Conference on Clean Combustion of Coal, Franklin Pierce College, New Hampshire, July 31-August 5, 1977.

3-48 Bowen, J. S., D. G. Lachapelle, and R. Stern, "Overview of EPA's NO_x Control Technology for Stationary Sources," presented at 67th Annual AIChE Meeting, December 1974.

3-49 "Analysis of the Proposed National Energy Plan" — Office of Technology Assessment, Congress of the United States, August 1977.

3-50 Ctvrtnicek, T. E., et al., "Evolution of Low-Sulfur Western Coal Characteristics, Utilization and Combustion Experience," Monsanto Research Corp., EPA 650/2-75-046, May 1975.

3-51 Shimizu, A. B., et al., "No Combustion Control Methods and Costs for Stationary Sources," Environmental Protection Technology Series, EPA-600/2-75-046, September 1975.

3-52 Bartick, H. A., et al., "The Production and Refining of Crude Shale Oil into Military Fuels," Final Report by Applied Systems Group, submitted to Office of Naval Research, Arlington, Va., August 1975.

3-53 Martin, G. B., "Evaluation of NO_x Emission Characteristics of Alcohol Fuels in Stationary Combustion Systems," presented at Joint Meeting, Western and Central States Sections, The Combustion Institute, April 21 and 22, 1975, San Antonio, Texas.

3-54 Hall, R. E., "The Effect of Water/Residual Oil Emulsions on Air Pollutant Emissions and Efficiency of Commercial Boilers," ASME 75-WA/APC-1, July 14, 1975.

3-55 Martin, G. B., "Environmental Considerations in the Use of Alternate Clean Fuels in Stationary Combustion Processes."

3-56 Martin, G. B., D. W. Pershing, E. E. Berkau, "Effects of Fuel Additives on Air Pollutant Emissions from Distillate Oil-Fired Furnaces," EPA, Office of Air Programs, AP-87, June 1971.

3-57 Shaw, H., "Reduction of Nitrogen Oxide Emissions from a Gas Turbine Combustor by Fuel Modifications," ASME Transactions, Journal of Engineering for Power, 95, 4, October 1973.

3-58 Altwicker, E. R., et al., "Pollutants from Fuel Oil Combustion and the Effects of Additives," Paper No. 71-14, 64th Annual APCA Meeting, Atlantic City, N. J., June 1971.

3-59 Barrett, R. E., et al., "Field Investigation of Emissions from Combustion Equipment for Space Heating," EPA R2-73-084a, June 1973.

3-60 Frey, D. J., "De-Ashed Coal Combustion Study," Combustion Engineering, Inc., October 1964.

3-61 Energy Research and Development Agency, "Proceedings of the Fourth International Conference on Fluidized Bed Combustion," McLean, Va., December 1975.

3-62 Jonke, A. A., et al., "Pollution Control Capabilities of Fluidized-Bed Combustion," AIChE Symposium Series No. 126, Vol. 68, 1972.

3-63 Chronowski, R. A., and B. Molayem, "NO_x Emissions from Atmospheric Fluidized-Bed Boilers," ASME 75-PWR-4, October 1975.

3-64 Pfefferle, W. C., et al., "CATATHERMAL Combustion: A New Process for Low-Emissions Fuel Conversion," presented at the 1975 ASME Winter Annual Meeting, Houston, Texas, ASME Paper No. 75-WA/FU-1.

3-65 Kesselring, J. P., et al., "Catalytic Oxidation of Fuels for NO_x Control from Area Sources," EPA Report, EPA-600/2-76-037, February 1976.

3-66 DeCorso, S. M., et al., "Catalysts for Gas Turbine Combustors — Experimental Test Results," paper presented at ASME Gas Turbine Conference and Products Show, New Orelans, March 1976, ASME Paper #76-GT-4.

3-67 Gerstin, R. A., "A Technical and Economic Overview of the Benefits of Repowering," paper presented at the Gas Turbine Conference and Products Show, Houston, Texas, March 2-6, 1975, ASME Paper #75-GT-16.

3-68 Ahuja, A., "Repowering Pays Off for Utility and Industrial Plants," Power Engineering, pp. 50-54, July 1976.

3-69 Stambler, I., "Repowering Gives Glendale Extra 75 MW and Lower Rates," Gas Turbine World, September 1977.

3-70 Robson, F. L., and A. J. Giramonti, "The Use of Combined-Cycle Power Systems in Nonpolluting Central Stations," JAPCA, Vol. 22, pp. 177-180, 1972.

3-71 Amos, D. J., et al., "Energy Conversion Alternatives Study (ECAS), Westinghouse Phase I Final Report, Volume V — Combined Gas Steam Turbine Cycles," NASA CR-134941, Volume V, 1976.

3-72 Papamarcos, J., "Combined Cycles and Refined Coal," Power Engineering, December 1976, pp. 34-42.

3-73 Ando, J. and B. A. Laseke, "SO_2 Abatement for Stationary Sources in Japan," EPA-600/7-77-103a, September 1977.

3-74 Stern, R., "The EPA Development Program for NO_x Flue Gas Treatment," In: Proceedings of the National Conference on Health, Environmental Effects, and Control Technology of Energy Use, EPA Report 600/7-76-002, February 1976.

3-75 Koutsoukos, E. P., et al., "Assessment of Catalysts for Control of NO_x from Stationary Power Plants, Phase I," Volume I, EPA-650/2-75-001-2, January 1975.

3-76 Muzio, L. L., J. K. Arand, and D. P. Teixeira, "Gas Phase Decomposition of Nitric Oxide in Combustion Products," In: Proceedings of the NO_x Control Technology Seminar, EPRI Special Report SR-39, February 1976.

3-77 "Technology and Economics of Flue Gas NO_x Oxidation by Ozone," EPA 600/7-76-003, December 1976.

3-78 "Nitric Acid from Ammonia," Hoechst-Uhde Corp. brochure (FWC 11 619), Englewood Cliffs, N.J.

3-79 Mayland, B. J., "The CDL/VITOK Nitrogen Oxides Abatement Process," Chenoweth Development Laboratory, Louisville, Ky.

3-80 "New System Knocks NO_x Out of Nitric," Chemical Week, September 3, 1975, pp. 37-38.

3-81 "NO_x Removal System Now Available," Wet Scrubber Newsletter, September 30, 1973, pp. 3-4.

3-82 Personal communication, Mr. Kenneth Ficek, Technical Service Manager, Carus Chemical, November 1977.

3-83 Mayland, B. J., "Application of the CDL/VITOK Nitrogen Oxide Abatement Process," presented at Sulfur and Nitrogen Symposium, Salford, Lancashire, U.K., April 1976

3-84 Mayland, B. J., and R. C. Heinze, "Continuous Catalytic Absorption for NO_x Emission Control," Chemical Engineering Process, Vol. 6, May 1973, pp. 75-76.

SECTION 4

LARGE FOSSIL FUEL COMBUSTION PROCESSES

Fossil fuel combustion in utility and industrial boilers and internal combustion (IC) engines account for about 80 percent of NO_x emissions from stationary sources (see Section 2). The large boiler category encompasses application to utility power generation and industrial process steam generators. Large IC engines are used predominantly for power generation and for pipeline pumping and encompass large bore reciprocating engines as well as continuous combustion gas turbine engines. This section summarizes the effectiveness, cost, user experience and energy and environmental impact of the implementation of NO_x controls on these equipment categories.

4.1 ELECTRICAL UTILITY BOILERS

Most of the nation's electricity is generated in large fossil-fueled central station power plants, which consist of high-pressure watertube boilers in the 100 to 1000 MW* range serving turbine-generators. Firing capacities of individual burners in utility boilers commonly have thermal inputs as high as 58 MW (200 x 10^6 Btu/hr). A 1000 MW* opposed wall-fired unit may require as many as 60 separate burners.

Although there are some differences among utility boiler designs in such factors as furnace volume, operating pressure, and configuration of internal heating transfer surface, the principal distinction is firing mode. This includes the type of firing equipment, the fuel handling system, and the placement of the burners on the furnace walls (see Section 2.3.1).

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*Electrical utility boilers are commonly described in terms of electrical output rating. This convention will be used throughout Section 4.1.

The total NO_x emitted in 1974 by the electric utility industry was 5.1 Tg (5.6×10^6 tons) or 41.9 percent of the total stationary source emissions. Coal-fired boilers accounted for approximately 68 percent of the total utility emissions. A more detailed emission breakdown is presented in Section 2. For reference, the ranges of uncontrolled NO_x emissions for three of the firing types are given in Table 4-1. Cyclone-fired boilers typically have the largest uncontrolled emissions, and tangentially-fired have the lowest (Reference 4-1).

4.1.1 Control Techniques

The NO_x control options for utility boilers include combustion modification, flue gas treatment, and fuel modification. The former has been the most successful and widely used option, and is described below for gas, oil, and coal-fired units. The other less popular and less developed options are discussed after combustion modification.

4.1.1.1 Combustion Modification

The general concept of combustion modifications as potential NO_x control techniques for stationary sources was discussed in Section 3.1. These techniques have been developed and refined in numerous laboratory test installations and in many successful field applications to commercial utility boilers.

Utility boilers, due to their importance as NO_x sources and their control flexibility, are the most extensively modified stationary equipment type. The selection and implementation of effective NO_x controls for a specific utility boiler is uniquely dependent on the furnace characteristics (i.e., geometry and operational flexibility), fuel/air handling systems and automatic controls, and to the potential for operational problems which may result from combustion modifications. The following discussion is, therefore, not intended to provide application guidelines, but rather to give a broad overview and evaluation of tested procedures.

Table 4-2 summarizes the status of combustion modification technology for NO_x control in utility boilers. The references cited in the table are bases for the remainder of the discussion in this section. The table also lists typical values of controlled emissions for the major modification techniques and two major firing types, tangential firing and wall firing.

Retrofit NO_x control implementation by combustion modification usually proceeds in several stages depending on the emission limits to be reached. First, fine tuning of combustion conditions by lowering excess air and adjusting the burner settings and air distribution is employed. If NO_x emission levels are still too high, the minor modifications, such as biased firing or burners out of service (BOOS) are implemented. Increased frequency of boiler washing increases flame heat

TABLE 4-1. RANGE OF UNCONTROLLED UTILITY BOILER NO_x EMISSIONS (Reference 4-1)

Firing Type	Emissions ng NO_2/J[a] (ppm at 3% O_2)		
	Gas[b]	Oil[b]	Coal[b]
Wall: Front Wall	66 - 357 (130 - 700)	140 - 308 (250 - 550)	258 - 517 (425 - 850)[c]
Opposed Wall	204 - 484 (400 - 950)	112 - 280 (200 - 500)	242 - 545 (400 - 900)[c]
Tangential	51 - 178 (100 - 350)	56 - 196 (100 - 350)	180 - 361 (300 - 600)
Cyclone	—	168 - 280 (300 - 500)	303 - 725 (500 - 1200)

[a] Heat input based on higher heating value of fuel

[b] Higher heat values: Gas = 41 MJ/Nm^3 (1100 Btu/standard ft^3)
No. 6 Oil = 42 kJ/g (18,000 Btu/lb)
Bituminous coal = 30 kJ/g (13,000 Btu/lb)

[c] For dry bottom furnaces. NO_x emissions from wet bottom furnaces can be as high as 910 ng/J (1500 ppm).

TABLE 4-2. SUMMARY OF COMBUSTION MODIFICATION TECHNIQUES FOR LARGE BOILERS[a]

Technique	Principle of Operation	Emission Rates (NO_x) NO2 Basis @ 3% O_2[b]	Limitations[c]	Existing Applications	Applications Planned for Next 5 Years	Reference
Overfire Air with Tangential Firing	Lower nozzles operated fuel rich yielding reduced O_2 level in primary zone and suppression of thermal and fuel NO_x	Gas: 100-150 ppm Oil: 125-225 ppm Coal: 250-400 ppm	Fouling of convective section; poor primary stage ignition; soot formation; possible load reduction	Retrofit of utility boilers, large industrial boilers, all new utility boilers	Inclusion of overfire air ports in new unit design	4-6 4-12
Overfire Air with Wall Firing	Biased burner firing or overfire air ports reduces O_2 level in primary flame zone and suppresses thermal and fuel NO_x	Gas: 200-300 ppm Oil: 250-350 ppm Coal: 400-500 ppm	Corrosion with coal firing, fouling of convective section.	Retrofit of utility boilers, large in dustrial boilers, new utility boilers	Inclusion of overfire air ports in new unit design	4-12 4-15
Flue Gas Recirculation	Recycled flue gas reduces primary flame temperature and suppresses thermal NO_x	Gas: 80-120 ppm (tangential) 250-350 ppm (wall firing) Oil: 150-220 ppm (tangential) 250-350 ppm (wall firing)	Reduced effect with coal, heavy oils; flame instability	Retrofit of gas and distillate oil utility boilers	Inclusion in design of large industrial boilers; not planned for coal	4-12 4-15
Low Excess Air firing	NO_x control through reduced O_2 level in primary flame zone	Gas: 200-250 ppm (tangential) 300-350 ppm (wall firing) Oil: 200-250 ppm (tangential) 300-350 ppm (wall firing) Coal: 350-450 ppm (tangential) 450-660 ppm (wall firing)	Unburned hydrocarbons, CO emissions at low levels of excess air; increased fouling	Routine use in utility boilers; limited use in industrial boilers	Application to commercial and industrial boilers as part of energy conservation programs	4-12 4-15

[a] Combined modifications are excluded; the NO_x control with combined modifications is generally less than the additive effects of the modifications applied singly.

[b] Emission rates cited are nominal values for average unit capacity and operating conditions; the range of available data is much wider than the values reported.

[c] More likely with modification to existing units than with new designs.

TABLE 4-2. SUMMARY OF COMBUSTION MODIFICATION TECHNIQUES FOR LARGE BOILERS[a] (Concluded)

Technique	Principle of Operation	Emission Rates (NO_x) NO_2 Basis @ 3% O_2[b]	Limitations	Existing Applications	Applications Planned for Next 5 Years	Reference
Low Air Pre-Heat	Reduced combustion air temperature yields lower flame temperature and lower NO_2	Little data	Reduced plant thermal efficiency	None	None	4-6 4-18
Water Injection	Reduced flame temperature, possible emulsion effect	Little data	Reduced thermal efficiency; severe operation problems with high level of water injection	None	None	4-5 4-7
Ammonia Injection	Chemically reduce NO_x in post flame region	30-80% reduction	Ammonia in stack gas, may limit load following ability, not tested for coal	Oil and gas prototype demonstration	Selected applications to oil and gas fired equipment	4-45 4-46 4-48
New Burner Designs	Controlled mixing of fuel/air yields control of thermal, fuel NO_x	Gas: 150-220 ppm Oil: 200-250 ppm Coal: 240-450 ppm	NO_x control through retrofit constrained by firebox configuration	Wall-fired boilers: new and retrofit	Inclusion in new unit design for utility and industrial boilers	4-12 4-43 4-44 4-47

[a] Combined modifications are excluded; the NO_x control with combined modifications is generally less than the additive effects of the modifications applied singly.

[b] Emission rates cited are nominal values for average unit capacity and operating conditions; the range of available data is much wider than the values reported.

removal thereby decreasing thermal NO_x (Reference 4-2). If still necessary, these minor modifications are followed by the major retrofits, including overfire air ports (OFA), flue gas recirculation (FGR), and new burners.

At present, more of these stages of control have been implemented for control of thermal NO_x than for fuel NO_x control. That is, FGR and staging are now commonly found in gas and oil-fired boilers, while coal-fired units are only just now entering the second stage of control.

The feasibility, effectiveness, and application technique of the modifications within each stage of control depend heavily on the fuel and firing type. For example, testing has shown that FGR does not significantly reduce fuel NO_x, so this technique is usually not cost-effective for coal-fired units. Also, such techniques as BOOS or OFA are implemented differently on wall-fired than on tangentially-fired units due to burner configuration and hardware differences.

The practical limits on the modifications are based initially on three subjective criteria: emission of other pollutants (i.e., CO, smoke, and carbon in flyash), onset of slagging or fouling and incipience of flame instability at the burner. When problems are encountered, implementation is halted and the situation reevaluated. Stack gas sampling for NO_x, CO, and O_2 is usually carried out concurrently during compliance tests. In the long term, the effects of the modification on such factors as burner condition, furnace slagging and corrosion, ability to change fuels, and boiler load are monitored to varying degrees.

The remainder of this section describes recent combustion modification experience on gas, oil and coal-fired boilers.

Gas-Fired Boilers

The highest degree of success in reducing NO_x by the application of combustion modifications has been obtained on gas firing. The reason for this effectiveness lies in the fact that all of these techniques reduce thermal NO_x, which is the only NO_x formation mechanism in gas combustion.

Low excess air operation has been shown to be extremely effective in lowering NO_x emissions from gas-fired boilers. An extensive 1971 study of NO_x reduction techniques applied to six wall-fired utility boilers showed reductions of 25 to 60 percent at full load. The NO_x reduction magnitude depends not only on final excess air level, but also on furnace design and firing method (Reference 4-3).

In 1972, a West Coast utility obtained a 23 percent NO_x reduction on a 750 MW* horizontally opposed unit as a result of lowering excess air. Off-stoichiometric firing and flue gas recirculation were subsequently implemented on this unit to achieve over 50 percent further reduction (Reference 4-4). In other early work a 33 percent NO_x reduction on a 250 MW* tangentially-fired utility boiler was obtained when the flue gas oxygen content was decreased from 3.9 percent to 0.6 percent (Reference 4-5). In most cases, LEA was implemented without serious flame stability problems, and a slight increase in thermal efficiency was noted.

From both full and pilot scale results, flue gas recirculation (FGR) has been proven effective for lowering NO_x formation from gas combustion. In general, NO_x reduction figures range from 20 to 60 percent for various boiler designs and load conditions. NO_x reductions are substantial up to 20 percent FGR; further recirculation yields only marginal additional reduction. Subscale testing has shown that the magnitude of NO_x reduction is mainly dependent on the amount of gas recirculated up to the point of incipient flame instability and other undesirable operating conditions. Some references which may be scanned for further details on FGR are References 4-3, 4-6, 4-7, and 4-8.

With gas firing, off-stoichiometric combustion (OSC) has been shown to be one of the most effective means of NO_x control and also one of the easiest to implement. Biased firing and burners out of service (BOOS) are the most frequently used and most effective OSC methods. Overfire air port operation achieves less reduction, particularly where biasing has already been implemented. NO_x reduction figures of 25 to 58 percent were obtained on wall-fired utility boilers ranging from 80 to 480 MW* when two-stage combustion was applied (Reference 4-3). Similar results were reported for gas-fired boilers in Southern California. The effectiveness of off-stoichiometric combustion with gas firing has been well validated and documented (References 4-3, 4-6, and 4-9).

The effectiveness of overfire air and flue gas recirculation on existing gas, tangentially-fired boilers is shown graphically in Figure 4-1. The bar chart shows the variation in uncontrolled emissions even among boilers of the same capacity and design. Emissions from five of the boilers that exceeded the EPA's standard of performance for new gas-fired sources, 86 ng NO_2/J (0.2 lb/10^6Btu), were reduced below the standard by either overfire air or FGR. The data also show a trend toward higher emissions in larger units. This is attributed to the increase in thermal NO_x formation due to the higher temperatures resulting from the higher volumetric combustion intensity used in larger boilers (Reference 4-6).

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*electrical output rating

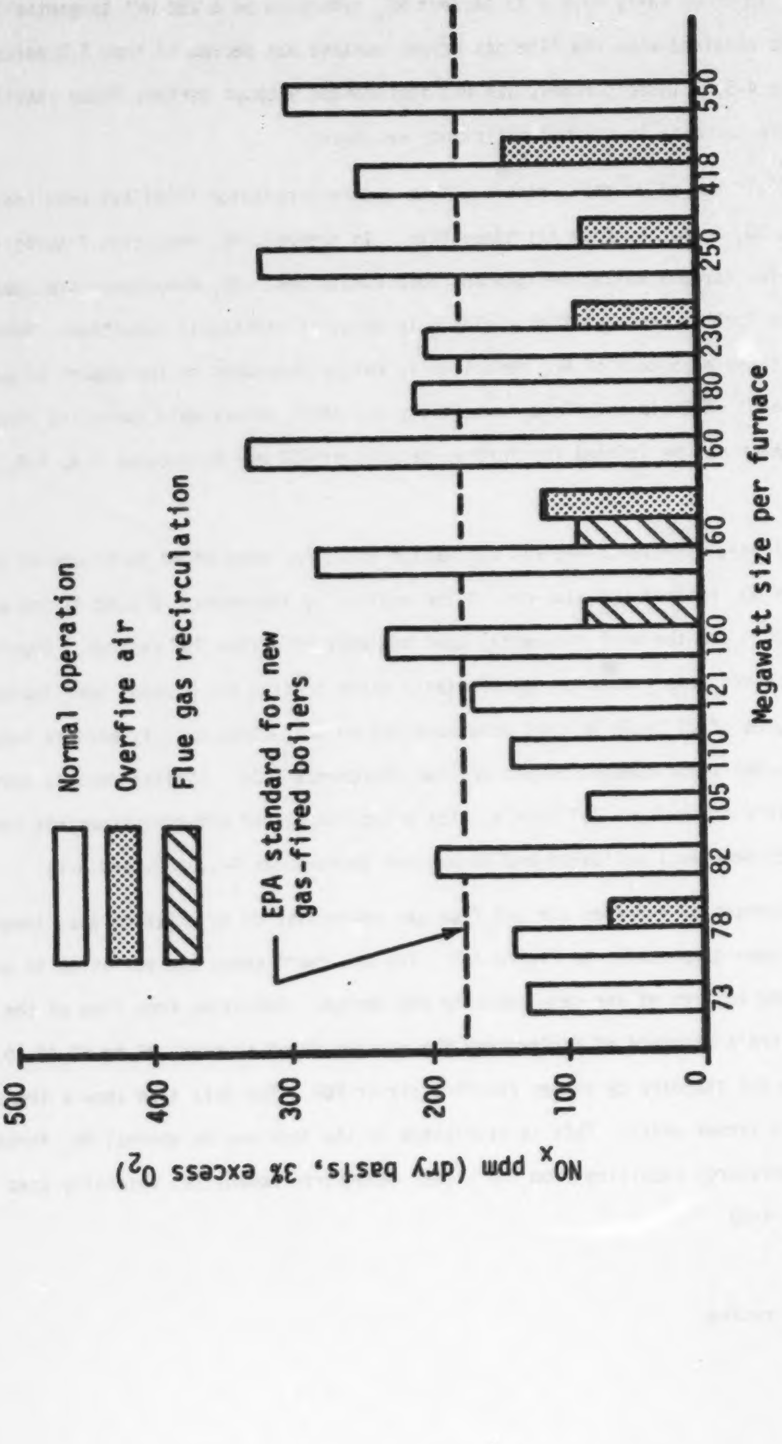

Figure 4-1. NO$_x$ emissions from gas, tangentially-fired utility boilers (Reference 4-6).

Figure 4-2 shows results from the modification of a 750 MW*, horizontally-opposed, wall-fired unit firing gas. At full load, a 90 percent NO_x reduction was obtained using the combination of staging and FGR. These results also show that load reduction is effective for NO_x control, but is not favored because of economic considerations (Reference 4-4). It should be noted that this 90 percent reduction is more a result of the extremely high uncontrolled NO_x emissions (1400 ppm) for this unit, than of any special control procedures used. For units with more moderate uncontrolled emissions, a 50 to 60 percent reduction is usually the upper limit.

Water injection into gas-fired utility boilers has been tested to a limited extent. A 50 percent maximum NO_x reduction was demonstrated at full load for a 250 MW* tangentially-fired unit when water was injected at a rate of 20 kg per GJ (45 lb/10^6 Btu) fired. Boiler convective section temperature increased by 139K (250F) and boiler efficiency dropped 5 percent. The economic penalties resulting from this method, as from reduced load or air preheat, make such techniques unattractive (Reference 4-5).

A significant amount of work has been done on optimizing gas burner design for low NO_x production. Of the three types of burners - spud, radial spud, and ring - the latter produce the least NO_x, while the spud type yields the highest NO_x formation. In addition, burners which produce controlled, low turbulence, flames have been found to form lower quantities of NO_x.

In summary, the effectiveness of NO_x controls for gas-fired utility boilers has been adequately explored. Further investigation may not be warranted because the number of large gas-fired utility and industrial boilers, small to begin with, is now declining rapidly due to the present natural gas supply shortage. For example, several West Coast utilities, the nation's largest users of gas for this purpose, reduced from about 70 percent gas-firing in 1972 to less than 10 percent in 1974. Low sulfur residual oil is the predominant fuel to replace gas on the West Coast.

Oil-Fired Boilers

Compared to gas-fired boilers, a generally poorer record of NO_x reduction has been compiled for oil-fired units. This is due largely to reduced operating flexibility. When firing residual oil, fuel NO_x becomes an important contribution to the total NO_x emission from a given unit, and the individual modifications are less effective and more complicated to implement. Nevertheless, substantial reductions have been achieved, in some instances as high as 60 percent on utility boilers.

The most popular NO_x reduction techniques for both new and existing oil-fired boilers include overfire air ports, BOOS, flue gas recirculation, and combinations of these techniques. Lowering

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*electrical output rating

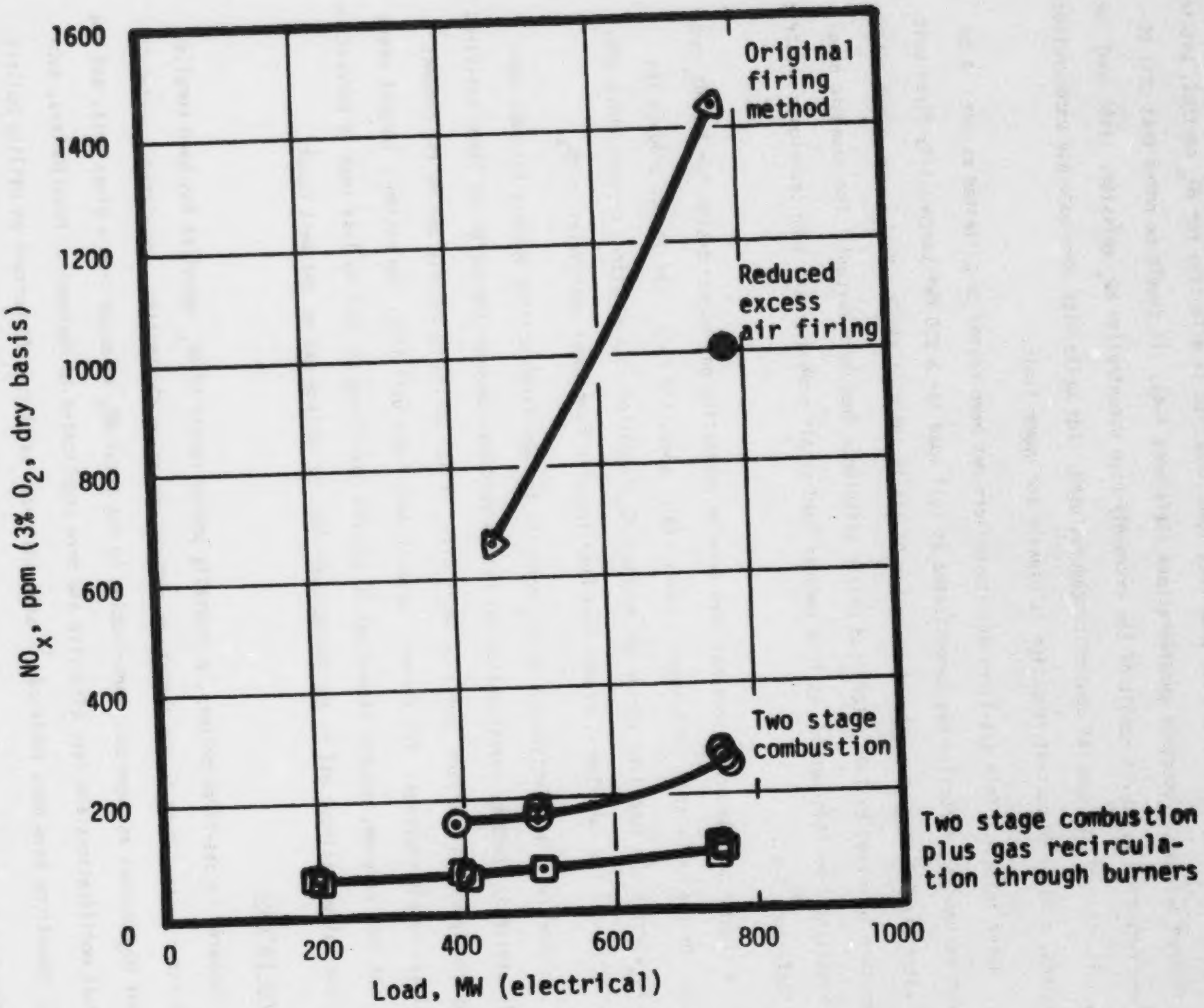

Figure 4-2. Effects on NO_x control methods on a gas, wall-fired utility boiler (Reference 4-4).

excess air is now considered a routine operating procedure and is incorporated in all new units. Overall response to the control techniques among boilers, even of the same size and design, can differ significantly.

For wall-fired units use of overfire air ports alone results in NO_x reductions of about 15 to 20 percent. For both wall- and tangentially-fired units, BOOS is implemented by removing from service several burners in the upper part of the firing pattern. This technique results in NO_x reductions of 25 to 35 percent. Flue gas recirculation, in which 15 to 25 percent of the combustion air is recirculated flue gas, has given NO_x reductions of 10 to 45 percent. However, control effectiveness is usually extended when FGR is combined with the other techniques. BOOS and FGR give total NO_x reductions of 40 to 60 percent, although derating is sometimes necessary to reach these levels (References 4-3 and 4-10).

The combined use of overfire air and BOOS operation reduces NO_x only marginally. Smoke thresholds are higher and excess air levels must be slightly increased, which cancels the effects of the overfire air. However, if boiler load is reduced, lower first stage stoichiometries are permitted and further NO_x reductions are achieved with BOOS and OFA.

The effectiveness of overfire air, flue gas recirculation, and their combination on existing oil, tangentially-fired boilers is shown graphically in Figure 4-3. Emissions from four of the boilers that exceeded the EPA's performance standard for new oil-fired sources, 129 ng NO_2/J, (0.3 lb/10^6 Btu) were reduced below the standard by use of either overfire air or FGR.

Figure 4-3 also shows the influence of fuel NO_x on the total NO_x production. Unlike the data for gas-fired units shown previously in Figure 4-1, there is no discernible trend toward higher emissions from larger units. Apparently, emissions are largely dependent on fuel nitrogen content. For example, the 160 MW (electrical) unit with an emission rate of 600 ppm was fired with a high nitrogen (1 percent) California residual oil, while the other two 160 MW units used oil with a nitrogen content of only 0.3 percent. The 45 percent difference in emissions can be attributed to higher fuel NO_x formation. In addition, the figure shows that FGR reduced total NO_x from the oil-fired boilers by only 30 percent, compared to 70 percent from gas-fired units. This is because FGR reduces thermal NO_x but is relatively ineffective on fuel NO_x.

Figure 4-4 shows results with oil firing from modifying the same wall-fired unit depicted in Figure 4-2. The combination of staging and FGR produced only a 50 percent NO_x reduction, compared to 90 percent on gas. Again, this difference is attributed mainly to the influence of fuel NO_x (Reference 4-4).

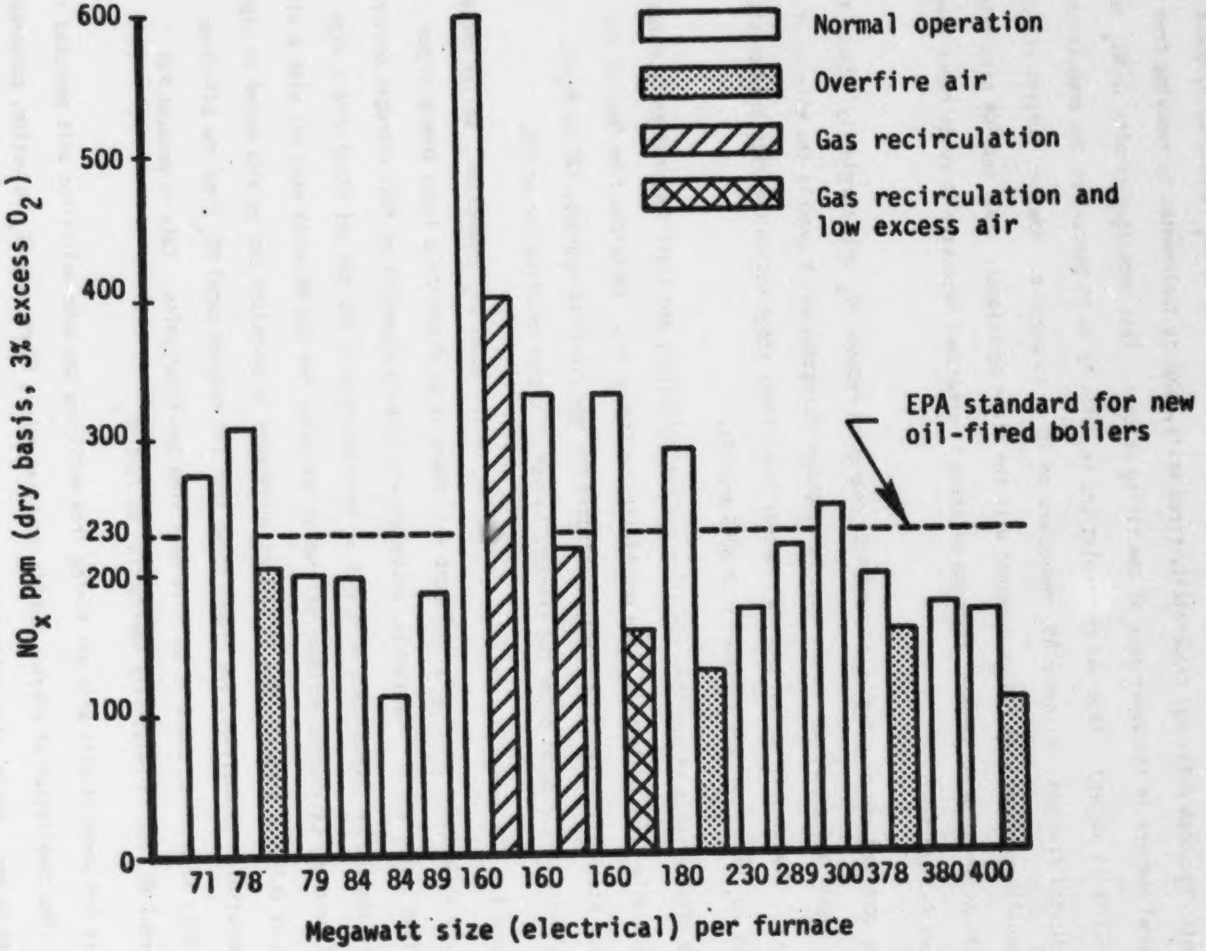

Figure 4-3. NO_x emissions from residual oil, tangentially-fired utility boilers (Reference 4-6).

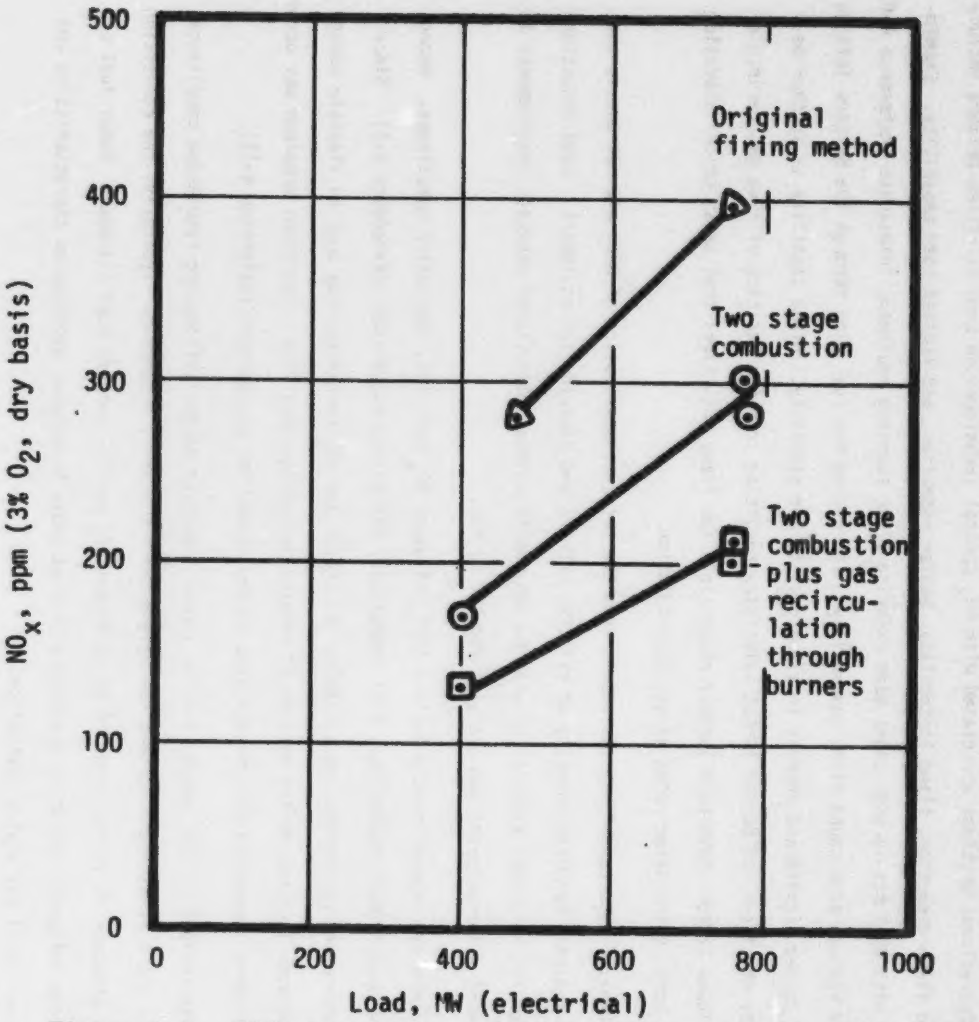

Figure 4-4. Effects of NO_x control methods on an oil, wall-fired utility boiler (Reference 4-4).

Some experimental work has been performed with injecting water into the combustion air of oil-fired boilers. Spraying water at a rate of about 0.6 kg per kg of oil reduced emissions about 40 percent. The effectiveness of FGR is increased when combined with water spraying, but the latter increases the minimum excess air requirement while FGR alone does not. In addition, the energy loss is significantly greater for water injection as compared to FGR to obtain equal NO_x reduction. For these reasons, water injection is not a popular NO_x control method.

Operational problems associated with NO_x control techniques on some oil-fired boilers include degraded flame detection, flame instability, boiler vibration, and limited load capability. Combining FGR with BOOS has in some cases made existing flame scanning equipment inadequate (Reference 4-6). BOOS and FGR can also cause flame instability. Increasing the fuel flow through the burners left in service causes significant changes in flame quality and stability. Flame stability is further degraded by the increased burner throat velocities resulting from the addition of flue gas recirculation. These factors have been largely responsible for flame pulsations that cause boiler vibration in some units using large rates of gas recirculation.

Limited load capability can result from the retrofit application of BOOS and FGR due to the limited fuel/air handling capacity of existing burners and distribution equipment. Load reductions of 10 percent have been experienced with burner modifications. Additional capacity requirements in the form of a forced draft fan are also imposed by FGR.

There are several subtle factors that influence NO_x emissions regulation compliance. Among them are operational flexibility, fuel properties, and boiler cleanliness (Reference 4-2). Since boiler operating conditions are variable, the chosen low NO_x operating mode must be flexible enough to allow some latitude during periods of adverse operating conditions. Equipment problems may occur somewhat more frequently due the the fine tuning needed for NO_x control (Reference 4-11).

Variations in fuel supply are the second important factor influencing regulation compliance. Residual oil fuel nitrogen content can vary between 0.2 and 1.0 percent. Typically, the conversion of fuel nitrogen is in the range of 20 to 40 ppm NO_x per 0.1 percent fuel nitrogen. Other fuel oil properties influence operating conditions such as smoke threshold, atomization characteristics and excess air level for stable combustion.

Boiler cleanliness appears to be another important factor influencing NO_x emissions. Indications are that up to a 50 ppm increase in NO_x emissions can be attributed to furnace deposits in the radiant section. This is attributable to higher flame temperatures needed as a result of the low radiant heat transfer condition incurred with deposits (Reference 4-2).

In general, an estimate of the boiler's actual operating conditions should be made in order to assess all factors that may influence regulation compliance. It is best to have at least a 25 to 35 ppm margin under average conditions (References 4-2, 4-3, 4-4, and 4-10).

Coal-Fired Boilers

The retrofit implementation of NO_x controls on coal-fired boilers is currently less widespread than on gas- and oil-fired units. Due to the continuing clean fuels supply shortage, however, the development of control for coal-fired units is receiving primary emphasis in the research and development programs of the Environmental Protection Agency's Industrial Environmental Research Laboratory at Research Triangle Park. Major developmental activity to date has been focused on achieving the level of control for new units mandated by the Standards of Performance for New Stationary Sources — 300 ng NO_2/J (0.7 lb/10^6 Btu). By contrast, the major activity for gas and oil-fired units has been on retrofit compliance with emission standards for existing units in NO_2-sensitive Air Quality Control Regions. Nearly all new utility boilers currently being installed, or on order, in the U.S. are designed to use coal as the primary fuel.

The combustion characteristics of a solid fuel such as coal are vastly different from either gas or oil, and the NO_x control strategy varies accordingly. For the cleaner fuels, thermal NO_x formation mechanism dominates; certain sets of combustion modification methods have been found to be well suited to suppress this problem. For coal, however, up to 80 percent of total oxides of nitrogen comes from fuel-bound nitrogen. Researchers have found that combustion modification methods that were effective on gas and oil firing either do not work as well or must be applied differently on coal-fired boilers. In addition, operational problems associated with the modifications, such as slagging, fouling, and carbon burnout, are more pronounced.

The most extensive series of tests performed on coal-fired boilers has been sponsored by the EPA and the Electric Power Research Institute. The combustion modification methods tested include lowering excess air, off-stoichiometric combustion, biased firing, a "low NO_x" burner, and flue gas recirculation. Coals tested include both Eastern and Western bituminous and Western sub-bituminous.

The sequence of combustion modification implementation is similar to that for gas and oil firing. First, the boiler is fine tuned by minimizing excess air to the threshold of excessive CO and unburned hydrocarbon formation. If the NO_x reduction obtained by such a procedure is inadequate, off-stoichiometric techniques, such as biased firing and burners on air only, may be utilized. The hardware retrofit methods are the last to be used. These include overfire air ports and "low NO_x" burners.

In field tests, existing wall-fired boilers under full load baseline operation generally produced NO_x emissions that exceeded the NSPS for new boilers. However, under modified operation using low excess air and staged firing, NO_x was reduced about 20 to 40 percent and the boilers were able to meet the new unit standard. Additional reductions were possible in some cases when the load was reduced about 20 percent. One 270 MW (electrical) wall-fired boiler, after being fitted with a specially-designed "low NO_x" burner, obtained a NO_x reduction of 35 percent (Reference 4-12).

Flue gas recirculation has also been tested on a wall-fired boiler (Reference 4-13). Applying 15 percent windbox FGR to a 560 MW (electrical) unit resulted in a 13 to 17 percent NO_x reduction under normal, air-rich, conditions. When applied in conjunction with OFA, FGR yielded a 7 percent NO_x reduction to augment the 33 percent reduction from OFA alone. The reduction obtained from FGR alone is, however, less than half of that normally obtained on oil firing. It appears that, due to the influence of fuel NO_x formation, FGR is generally less effective for coal firing than for gas and oil firing. FGR may be justified if minor emission reductions (i.e., "trimming") are necessary to achieve compliance with a stringent emission standard for existing units.

Under baseline conditions, tangentially-fired boilers usually emit less NO_x than wall-fired boilers. For example, of the 16 units shown in Figure 4-5, 10 meet the NSPS with no modifications. For those that do not meet the regulation, overfire air, burner staging, and low excess air techniques can be used to reduce NO_x by an average of 40 percent.

A measure of the degree of control implemented with off-stoichiometric combustion is given by the value of the first stage burner stoichiometry. Figure 4-6 shows the relationship of NO_x reduction with stoichiometry to the active burners for 13 tangential, coal-fired boilers (References 4-3, 4-12, 4-14, 4-15, 4-16, and 4-17). The best-fit line illustrates that NO_x emissions in general are reduced approximately 140 ppm for each 10 percent reduction in burner stoichiometry. It was also discovered that an optimum burner tilt angle exists from a NO_x formation standpoint. Horizontal burner operation reduced NO_x emissions by 18 percent, while lowering burner tilt to -26 percent increased NO_x emissions to 9 percent above baseline operation (Reference 4-12).

Several utility boiler tests have been conducted using the combined firing of gas/coal and oil/coal as a NO_x reduction strategy. Tests on the former mixture were conducted on a 130 MW (electrical) tangential unit. Firing with 80 percent of the heat release from coal reduced NO_x by an average of 30 percent, while firing with 60 percent coal and 40 percent gas resulted in a 32 percent NO_x reduction from 100 percent coal firing. The data indicate that replacing coal with gas fuel lowers NO_x in the direction of 100 percent gas firing, but the relationship is not linear.

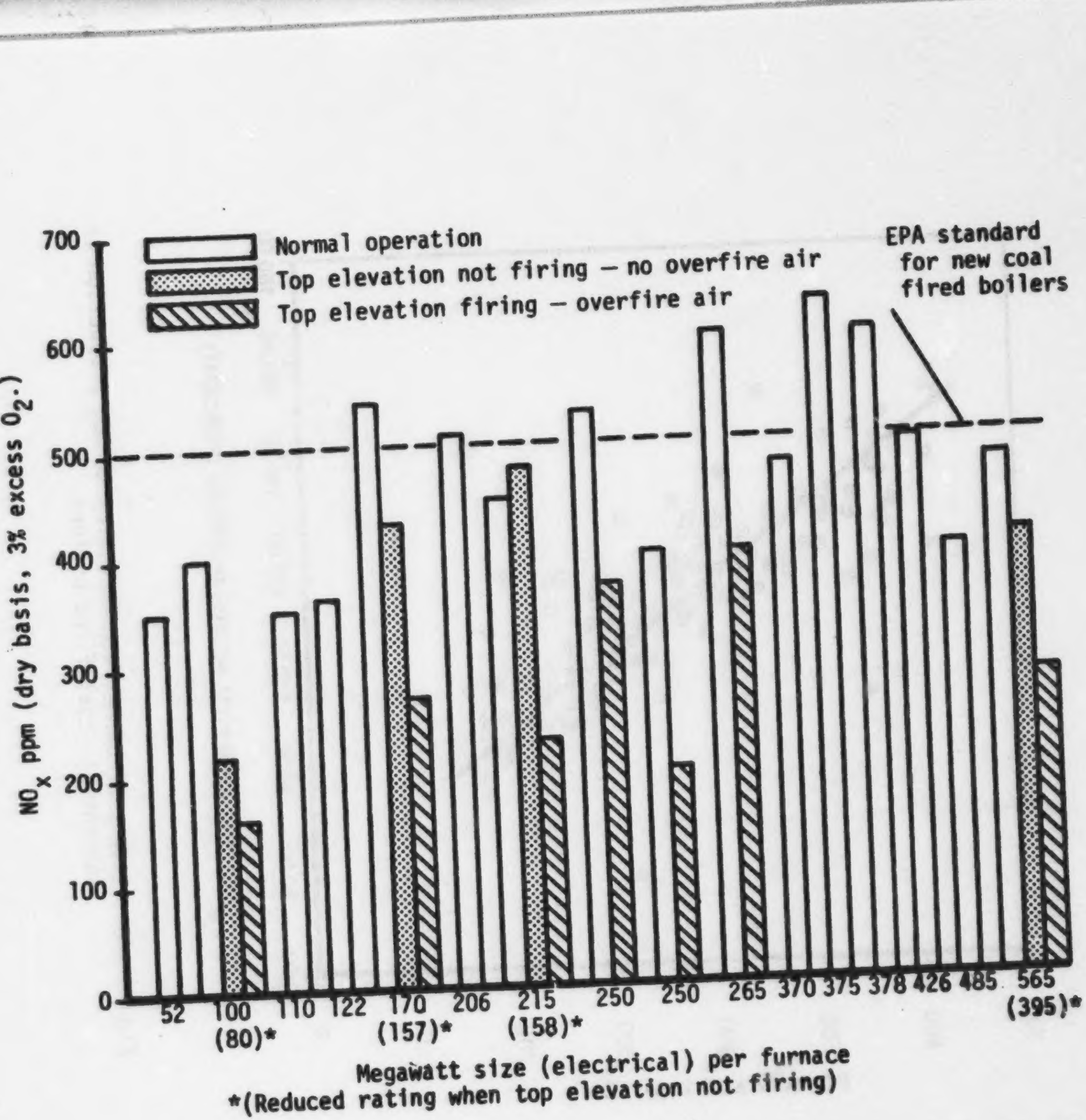

Figure 4-5. NO_x emissions from tangential, coal-fired utility boilers (Reference 4-6).

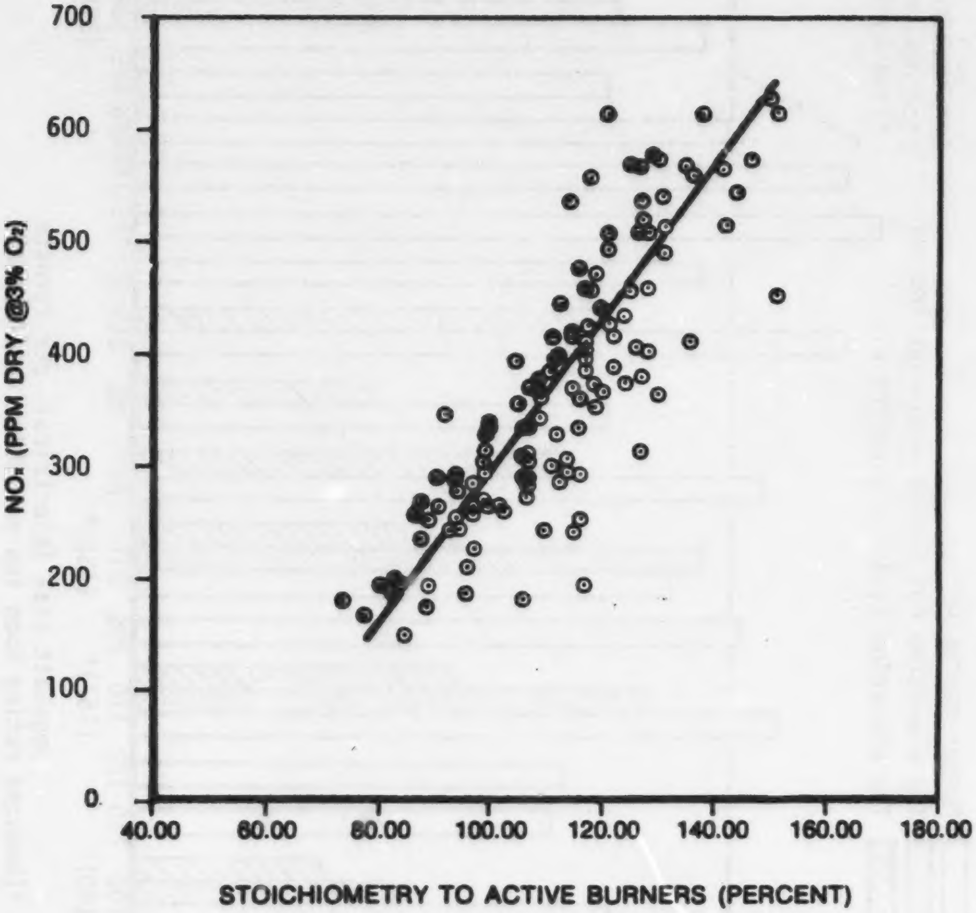

Figure 4-6. Effect of burner stoichiometry on NO_x production in tangential, coal-fired boilers.

Similar results were obtained with the oil/coal mixed fuel. Further NO_x reductions were possible when mixed fuel firing was combined with techniques such as lowering excess air, off-stoichiometric combustion, and reduced load (Reference 4-12).

Throughout the developmental field tests, attention was given to the potential side effects of low NO_x operation. Excessive smoke and CO levels generally limit the extent to which the burners are fired fuel-rich. The fuel-rich conditions can lead to flame instability, and the reducing atmosphere in the primary combustion zone can accelerate tube corrosion and slagging (Reference 4-18). One utility company reported experience with retrofit biased firing on a coal-fired boiler. The problems included increases in carbon losses, decreases in boiler efficiency of about one percentage point at all load levels, and increases in tube wastage on the sidewall near the biased burners (Reference 4-19). The EPA is conducting long-term field tests to determine the extent to which OSC accelerates tube wastage. Corrective measures to suppress tube wastage are also being examined. One utility boiler manufacturer uses a "curtain air" oxidizing atmosphere at the tube walls to suppress wastage (Reference 4-20).

4.1.1.2 Flue Gas Treatment

The major NO_x control emphasis in the United States has been on process modification since it permits the construction of new equipment that can meet existing emission standards. Due mainly to economic penalties, a less intensive effort has been devoted to removing nitrogen oxides directly from flue gases. However, faced with emission standards 20 to 40 percent more stringent than those in the U.S., Japanese industry has been much more interested in flue gas treatment (FGT) and has several major pilot plants and full-scale plants in operation. The major application of flue gas treatment in Japan has been to utility boilers and the larger combustion and noncombustion industrial point sources of NO_x. More inexpensive alternatives, such as process modifications, will continue to be used for smaller combustion sources of NO_x, although regulations could eventually require the use of FGT as well.

As described in Section 3.2, the two FGT process routes can be categorized as dry processes (reduction) and wet processes (oxidation followed by scrubbing). In Japan, dry processes are the more popular of the two types, and these usually involve the use of the selective catalytic reduction process (SCR). Table 4-3 shows the SCR processes on commercial and pilot plants in operation or under construction in Japan.

Most of the larger installations treat only "clean" exhaust gas from the combustion of gaseous fuels. However, two large plants being constructed by Sumitomo Chemical and Hitachi

TABLE 4-3. MAJOR JAPANESE DRY FGT INSTALLATIONS (Selective Catalytic Reduction) (Reference 4-21)

Process Developer	Capacity (Nm^3/hr)	Source of Effluent	Completion Date
Sumitomo Chemical	30,000	Oil-fired boiler	Jul 1973
Sumitomo Chemical	200,000[a]	Heating furnace	May 1974
Sumitomo Chemical	250,000[a]	Heating furnace	Mar 1975
Sumitomo Chemical	100,000[a]	Gas-fired boiler	Feb 1975
Sumitomo Chemical	200,000[a]	Gas-fired boiler	Feb 1975
Sumitomo Chemical	200,000[a]	Heating furnace	Mar 1975
Sumitomo Chemical	250,000	Oil-fired boiler	May 1976
Sumitomo Chemical	300,000	Oil-fired boiler	May 1976
Hitachi Shipbuilding	5,000	Oil-fired boiler	Nov 1973
Hitachi Shipbuilding	350,000	CO-fired boiler	Nov 1975
Hitachi Shipbuilding	440,000	Oil-fired boiler	Nov 1975
Tokyo Electric-Mitsubishi H.I.	10,000[a]	Gas-fired boiler	Jan 1974
Kurabo	5,000	Oil-fired boiler	Nov 1973
Kurabo	30,000	Oil-fired boiler	Aug 1975
Kansai Electric-Hitachi Ltd.	4,000	Oil-fired boiler	Jan 1975
Chubu-IHI-Mitsui Toatsu	8,000	Oil-fired boiler	Oct 1974
Chubu-MKK	100	Oil-fired boiler	Oct 1974
Mitsubishi H.I.	4,000	Oil-fired boiler	Dec 1974
Kobe Steel	600	Sintering plant	May 1974
Mitsui Toatsu	1,000[a]	Gas-fired boiler	Oct 1973
Mitsui Toatsu	3,000	Oil-fired boiler	Oct 1974
Mitsui Toatsu	4,000[a]	Gas-fired boiler	Oct 1974
Mitsui Toatsu	8,000[a]	Gas-fired boiler	Jun 1974
Hitachi Ltd. - Mitsubishi P.C.	150,000	Oil-fired boiler	Dec 1975
Hitachi Ltd.	350,000	Coke oven	Oct 1976
Ube Industries	10,000	Oil-fired boiler	Jan 1975
Mitsui S.B. - Mitsui P.C.	200,000	Oil-fired boiler	Sep 1975
Mitsui S.B. - Mitsui P.C.	240,000	Oil-fired boiler	Aug 1976
MKK - Santetsu	1,500	Oil-fired boiler	Dec 1974
MKK - Santetsu	1,000	Coke oven	Mar 1975
MKK - Santetsu	15,000	Oil-fired boiler	Jun 1976
Seitetsu Kagaku	15,000	Oil-fired boiler	Jun 1975
Japan Gasoline	50,000	Heating furnace	Nov 1975
Japan Gasoline	70,000	CO boiler	Mar 1976
Asahi Glass	70,000	Glass furnace	Apr 1976

[a] Clean gas; others are for dirty gas

Shipbuilding companies will treat "dirty" gas (containing SO_x and particulate) from oil-fired sources. A pilot plant treating dirty gas (oil-fired) has been operated by Sumitomo for over 4,000 hours reportedly without serious problems. Electrostatic precipitators remove dust and prevent contamination of the catalyst. More than 85 percent NO_x removal has been achieved (Reference 4-21).

Several EPA contractors have investigated SCR on both the lab and pilot scales. Emphasis was on technical and economic assessment of various catalytic processes, using both noble and nonnoble catalyst systems. These tests achieved NO_x reduction of 60 to 95 percent at inlet concentrations of 250 to 1000 ppm. They also indicated that platinum is not a satisfactory catalyst for flue gases containing SO_2.

Although selective catalytic reduction has been the most widely used and investigated dry FGT process, selective noncatalytic reduction of NO_x using ammonia has also been demonstrated commercially in Japan. NO_x reductions of 70 percent have been reported. Investigation of this technique is underway in the U.S. as well. Barriers to its use on steam generator exhaust include reducing agent injection problems, load following, byproduct emissions, and high reducing agent use and cost. The attractiveness of this technique may improve as more accurate assessment of these problems are developed (References 4-22 and 4-23).

Wet systems generally have not been as popular as dry processes. Major disadvantages of wet systems are (1) the need for expensive oxidizing agents and/or energy input in proportion to the quantity of NO_x removed, (2) generation of unmarketable byproducts, (3) waste water production, and (4) requirement of prior SO_2 removal to reduce the consumption of NO_x-removal chemicals. Its potential major advantage, however, is simultaneous NO_x and SO_x removal.

As with the dry process, most of the research, development and demonstration of wet processes has been conducted in Japan (Reference 4-21). In 1975, there were 12 different wet processes being developed in Japan at pilot plants and small commercial plants (100 to 25,000 cubic meters per hour). The largest systems reportedly are treating 32,000 to 1,000,000 cubic meters per hour of flue gas. No firm data are available as to NO_x removal efficiencies, but the range appears to be from 60 to 90 percent. Table 4-4 lists plants in Japan using wet FGT systems.

Two of these processes, the Chiyoda 102 and the Mitsubishi Heavy Industries Systems, are relatively simple extensions of well-established flue gas desulfurization (FGD) technology. Both processes are attractive from the standpoint of simultaneously removing SO_x and NO_x. However, both require the use of ozone. Ozone production for application to coal-fired flue gas is expected to require up to approximately 10 percent of the power plant electrical output. When added to the

TABLE 4-4. MAJOR JAPANESE WET FGT INSTALLATIONS (Reference 4-21)

Process Developer	Type of Process	Capacity, Nm^3/hr	Source of Effluent	Completion Date	By-product
Sumitomo Metal Fuji Kasui (Moretana)	Redox	62,000	Oil-fired boiler	Dec 1973	$NaNO_3$, NaCl Na_2SO_4
Sumitomo Metal Fuji Kasui (Moretana)	Redox	100,000	Metal heating furnace	Dec 1974	$NaNO_3$, NaCl Na_2SO_4
Sumitomo Metal Fuji Kasui (Moretana)	Redox	39,000	Oil-fired boiler	Dec 1974	$NaNO_3$, NaCl Na_2SO_4
Chiyoda	Redox (102 process)	1,000	Oil-fired boiler	1973	Gypsum, $Ca(NO_3)_2$
Osaka Soda	Redox	60,000	Oil-fired boiler	Mar 1976	$NaNO_3$, NaCl Na_2SO_4
Shirogane	Redox	48,000	Oil-fired boiler	Aug 1974	Na_2SO_4, $NaNO_3$
Mitsubishi H.I.	Redox	2,000	Oil-fired boiler	Dec 1974	Gypsum, N_2
Ishikawajima H.I.	Redox	5,000	Oil-fired boiler	Sep 1975	Gypsum, N_2
Tokyo Electric Mitsubishi H.I.	Oxidation absorption	2,000	Gas-fired boiler	Dec 1973	HNO_3
Tokyo Electric Mitsubishi H.I.	Oxidation absorption	100,000	Gas-fired boiler	Oct 1974	HNO_3
Kawasaki H.I.	Oxidation absorption	5,000	Coal-fired boiler	Dec 1975	Gypsum, $Ca(NO_3)_2$
Mitsubishi Metal MKK, Nihon Chem.	Absorption oxidation	4,000	Oil-fired boiler	Dec 1974	KNO_3
Kobe Steel	Absorption oxidation	1,000	Iron ore sintering furnace	Dec 1973	Gypsum, N_2
Kobe Steel	Absorption oxidation	50,000	Iron ore sintering furnace	Mar 1976	Gypsum, N_2
Nissan Engineering	Absorption oxidation	1,800	Pickling	Jul 1973	$NaNO_2$
Nissan Engineering	Absorption oxidation	3,000	HNO_3 plant	Mar 1975	$NaNO_3$, NO
Hodogaya	Absorption oxidation	4,000	Iron ore sintering furnace	Oct 1975	$NaNO_3$, NaCl
Chisso Corporation	Reduction	300	Oil-fired boiler	1974	$(NH_4)_2SO_4$
Mitsui S.B.	Reduction	150	Oil-fired boiler	1974	H_2SO_4, N_2
Asahi Chemical	Reduction	600	Oil-fired boiler	1974	Gypsum, N_2
Kureha Chemical	Reduction	5,000	Oil-fired boiler	Apr 1975	Na_2SO_4, N_2

power requirement of the FGD portion of these processes, this energy consumption may render wet simultaneous SO_x/NO_x processes impractical for commercial use.

In general, therefore, wet NO_x FGT systems cannot compete with dry selective catalytic reduction where simple NO_x control is involved. For coal-fired applications where high dust loadings and SO_2 removal are involved, it is not as yet clear whether dry FGT combined with conventional FGD processes will be cheaper than wet simultaneous SO_x/NO_x systems. Other dry simultaneous SO_x/NO_x systems, such as the Shell and the Sumitomo Shipbuilding processes, may also prove to be cheaper than the wet simultaneous processes. At present, the Shell process is being commercially applied on a 40 MW (electrical) oil-fired boiler in Japan and is being piloted in the U.S. on a 0.6 MW (electrical) flue gas stream from a coal-fired boiler. The Sumitomo Shipbuilding process is being tested on an oil-fired boiler in Japan.

In summary, wet FGT processes are more expensive and less well developed than dry processes. Considering their cost and complexity, it is doubtful that wet processes would be receiving any development attention in Japan were it not for the potential for simultaneous SO_x and NO_x removal (Reference 4-65).

4.1.1.3 Fuel Switching

The aim of this technique is to switch the combustion system to a fuel with a reduced nitrogen content (to suppress fuel NO_x) or to one that burns at a lower temperature (to reduce thermal NO_x). Switching decisions are based on the knowledge that solid fuels generally contain more organically-bound nitrogen than liquid fuels, and gaseous fuels are usually nitrogen-free. Coal-fired utility boilers, unless they already have a dual fuel capability, can be converted either to oil or gas. Likewise, oil-fired boilers can be switched to gas fuel. Due to design limitations, however, the reverse order of these conversions is generally not practical.

During the 1960's and early 1970's many Eastern and Midwestern U.S. coal-fired utility boilers were converted to oil and/or gas in response to tightened particulate and SO_2 emission standards. This trend was attractive from a NO_x control standpoint for two reasons. First, liquid and gaseous fuel firing provides more flexibility for implementing combustion modification techniques. Second, fuels containing less sulfur generally contain less nitrogen also, which serves to reduce fuel NO_x.

Despite the superiority of oil- and gas-fired NO_x control, the economic considerations in fuel selection are dominated by the current clean fuel shortage. Existing utility boilers are currently returning to coal, and the trend for new utility and industrial boilers is strongly toward the use of coal as well. Fuel switching to natural gas or low nitrogen oil is, therefore, not a promising short-term option.

A promising long-range option is the use of synthetic fuels derived from coal. Candidate fuels include lower Btu gas (3.7 to 30 MJ/Nm^3, or 100 to 900 Btu/scf) and synthetic liquids or solids. Although these fuels would have all the emission control advantages of conventional clean fuels, there are several disadvantages associated with them. First, economic considerations favor the placement of both the gasifier and the power cycle at the coal minehead. This fact eliminates existing utility boilers without an onsite coal supply as users of lower-Btu gas. Second, the cost of required equipment modification to lower-Btu gas is high, ranging from $5 to $15/kW*. Third, although synthetic oil can be transported like conventional oil, the coal conversion process is highly, and perhaps prohibitively, expensive (Reference 4-24, 4-25).

In general, the feasibility of coal-derived fuel switching is dependent on the cost tradeoff between the coal conversion route and more conventional means of controlling the criteria pollutants (i.e., gas cleaning). The economics of the former alternative are not well defined at present and will not be clear until the ongoing studies and pilot projects are completed (Reference 4-26).

4.1.1.4 Fuel Additives

The basis of this control technique was covered previously in Section 3.1.4. In general, fuel additives are not effective. Most of the additives that have been tested do not decrease NO_x emissions, and some that contain nitrogen actually increase NO_x formation. Several additives containing metallic compounds were found to promote the catalytic decomposition of NO and N_2. However, serious operational difficulties, high cost, and the presence of the additive as a pollutant in the exhaust made these additives unattractive (Reference 4-27, 2-28).

Other fuel additives investigated recently are intended to prevent boiler tube fouling. Use of these additives could conceivably allow a further decrease in excess air which would reduce NO_x formation. However, the emission reduction from this method is quite limited and the cost-effectiveness is likely to be poor (Reference 4-29).

4.1.2 Costs

The cost of implementing the preceding NO_x reduction techniques is basically the sum of the initial capital cost and annual operating cost (which includes any cost savings). The following discussion will center on the costs of reducing NO_x from utility boilers by combustion modification and flue gas treatment. In several cases the costs presented are for combined NO_x controls. Generally, the effectiveness of combined NO_x controls is not equal to the sum of the individual effects of each control. Likewise the cost of combined controls is not the sum of the costs of single controls. The cost of fuel additives is not discussed due to its status as an unattractive option and to a general lack of cost data. Fuel switching economics are similarly not treated in this discussion.

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*electrical output

4.1.2.1 Combustion Modification

Much of the pioneering work on evaluating the cost effectiveness of combustion modification in full-scale combustion equipment has been performed on utility boilers. Correspondingly, the related costs of these modifications have been fairly well documented compared to other source types. One of the earliest efforts of this kind was attempted by Esso Research Labs in 1969 (Reference 4-30). Based on estimates for the capital, annual, and operating costs, the Esso report presented the results of a cost effectiveness study performed for NO_x control on utility boilers by means of combustion modification. Since 1969, however, it has been revealed that a wide variation in the effectiveness of the control techniques among boilers exists. This problem will require that continuing cost-effectiveness evaluations be done on an individual boiler basis.

Data from Combustion Engineering

The most recent cost data were published in Reference 4-31 for new and existing tangential, coal-fired utility boilers. These data are summarized in Figures 4 - 7a and b. The cost range curves were derived from estimates developed under an EPA-sponsored contract involving the reduction of NO_x from both new and existing tangential coal-fired utility boilers. The costs are for the combined use of overfire air ports and low excess air firing, as this is the preferred control system for tangential, coal-fired boilers. Capital costs were projected over a unit size range of 25 to 1000 MW*. The corresponding annual operating costs for 500 MW* units was 0.006 mills/kWh for a new unit and 0.021 mills/kWh for existing units. Figure 4-7a applies to new unit designs with heating surfaces adjusted to compensate for the resultant changes in heat transfer distribution and rates. Figure 4-7b applies to existing units with no change in heating surface, as these changes must be calculated on an individual unit basis.

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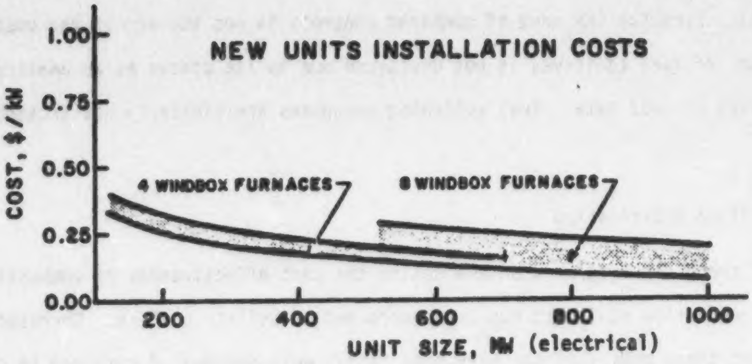
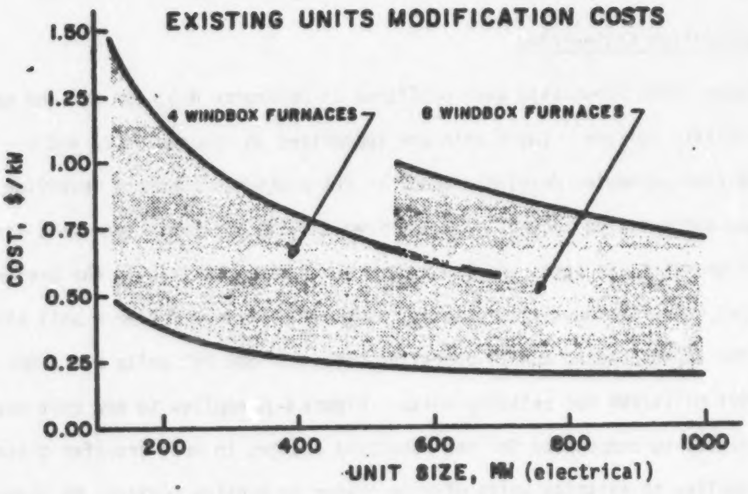
*electrical output rating



a) New boilers



b) Existing boilers

Figure 4-7. 1975 Capital cost of overfire air for tangential, coal-fired boilers (Reference 4-27).

It is readily observed that the cost ranges for existing units vary more widely than for new units. This is due to the variations in unit design and construction which can either hinder or aid the installation of a given NO_x control system.

Above approximately 600 MW*, single cell-fired boilers exceed a practical size limit and divided furnace designs are utilized. Since a divided tangentially-fired furnace has double the firing corners of a single cell furnace, the costs increase significantly.

It should be kept in mind that although these cost data for utility boilers were developed for tangentially coal-fired boilers, it is felt that the range of costs presented should also be applicable to wall-fired boilers burning coal. Additionally, the cost for similar combustion modification on gas and oil-fired utility boilers should be no higher than for the coal-fired units.

The cost of reducing low excess air was not investigated since there is generally no significant additional cost for modern units or units in good condition. However, some older units may require modifications such as altering the windbox by addition of division plates, separate dampers and operators, fuel valving, air register operators, instrumentation for fuel and air flow and automatic combustion controls.

Data from EPA

Table 4-5 shows estimated investment costs for low excess air (LEA) firing on utility boilers requiring modifications (Reference 4-1). These costs can vary depending on the actual extent of the required modification and are only provided as guidelines. As unit size increases, the cost per kW decreases since the larger units typically have inherently greater flexibility and may require less extensive modification.

The use of low excess air firing reportedly increases boiler efficiency by 0.5 to 5 percent. Additional savings may result from decreased maintenance and operating costs. Consequently, investment costs may be offset in fuel and operating expenses.

TABLE 4-5. 1974 ESTIMATED INVESTMENT COSTS FOR LOW EXCESS AIR FIRING ON EXISTING BOILERS NEEDING MODIFICATIONS

Unit Size (MW*)	Investment Cost ($/kW*)	
	Gas and Oil	Coal
1000	0.12	0.48
750	0.16	0.51
500	0.21	0.55
250	0.33	0.64
120	0.53	0.73

*electrical output rating

Data from the Pacific Gas and Electric Company

As an example of the manner in which the costs for combustion modification may vary among individual existing units, several case studies are presented in Table 4-6. The numbers shown are the costs incurred by the Pacific Gas and Electric Company during a program to bring six units into compliance with local NO_x emission regulations. For the most part, the conversions involved the combination of windbox flue gas recirculation and overfire air ports. The average cost of the modifications is about $10/kW* (Reference 4-32).

Data from the Los Angeles Department of Water and Power

Another West Coast electric utility company, the Los Angeles Department of Water and Power (LADWP), has had extensive experience in implementing NO_x control techniques on its gas- and oil-fired boilers. The techniques currently utilized by the Department include burners out of service (BOOS), overfire air ports, and low excess air. Although the units are operated with the lowest excess air possible, it has been found that when LEA is combined with other reduction methods, excess air levels must be increased beyond those normally required.

The Department's data indicate a unit efficiency decrease of approximately one percent attributable to BOOS operation. As has been found by other operators, LEA tended to increase efficiency slightly: a one percent decrease in excess oxygen increased efficiency by about 0.25 percent. Properly retrofitted, overfire air had no effect on efficiency.

The NO_x control costs incurred by LADWP are shown in Table 4-7 for four different units. The figures for the BOOS techniques reflect the R&D costs that necessarily precede the retrofit. All costs include the labor required to implement the control methods, and are, therefore, installed equipment costs. The very low expense associated with overfire air on the B&W 235 MW* unit is due to the base year of the estimate (1964 to 1965) and to the fact that this modification was included in the original boiler design.

The overfire air costs for the B&W 235 MW* unit lie in the low range of the appropriate band of costs in Figure 4-7b. The LADWP boilers were, for the most part, modified without much difficulty, and the associated costs probably represent the lower limits of the costs for the three NO_x reduction techniques implemented (Reference 4-33).

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*electrical output rating

TABLE 4-6. 1975 INSTALLED EQUIPMENT COSTS FOR EXISTING PACIFIC GAS AND ELECTRIC RESIDUAL OIL-FIRED UTILITY BOILERS (Reference 4-32)

Unit Name	Design Type	Year Online	Electrical Capacity (MW)	Modification Cost ($$10^6$)	$/kW	Year Modified	Type of Modification
Pittsburg #7	CE tangentially-fired, divided	1972	730	6.2	8.5	1975	Windbox FGR, Overfire Air ● Two new 5000 hp FGR fans ● FGR ducting (17% FGR) ● OFA port installation ● No new burner safeguard system
Pittsburg #5 and #6	B&W opposed-fired	1964	330 (each)	7.8 (both)	11.8	1975	Windbox FGR, Overfire Air ● Transferred two FGR fans from other units ● FGR ducting (17% FGR) ● New hopper ● OFA port installation; one for each burner column ● New burner safeguard system; computer, NO_x control board, O_2 controls on dampers, flame scanners
Contra Costa #9 and #10	B&W opposed-fired	1965	345 (each)	6 (both)	8.7	1975	Windbox FGR, Overfire Air ● New FGR fans (1 ea.) (17% FGR) ● Nominal amount of new ducting to windbox ● OFA port installation
Potrero #3	Riley turbo-fired	1972	206	3.5	17	1975	Windbox FGR, Overfire Air ● New FGR fan (17% FGR) ● OFA port installation, nominal amount of ducting ● New burner safeguard system, NO_x control board, computer
Moss Landing #6-1 and #7-1	B&W opposed-fired	1968	750 (each)	2.8 (both)	1.8	1971	Windbox FGR, Overfire Air ● Existing temperature control FGR fans replaced with larger fans ● New flame scanners

TABLE 4-7. LOS ANGELES DEPARTMENT OF WATER AND POWER ESTIMATED INSTALLED 1974 CAPITAL COSTS FOR NO_x REDUCTION TECHNIQUES ON GAS- AND OIL-FIRED UTILITY BOILERS (Reference 4-33)

Unit Capacity (MW)	Unit Type	NO_x Reduction Technique	Implementation Method	Estimated Cost ($)	$/kW
180	C.E. wall-fired	BOOS	Retrofit	67,400	0.38
		LEA	Retrofit	28,900	0.16
235	C.E. wall-fired	BOOS	Retrofit	75,200	0.32
		LEA	Retrofit	28,900	0.12
235	B&W Opposed-fired	BOOS	Retrofit	75,000	0.32
		Overfire air	Original Design	14,000[a]	0.06
		LEA	Retrofit	28,900	0.12
350	B&W Opposed-fired	BOOS	Retrofit	266,000	0.76
		Overfire air	Retrofit	100,600	0.29
		LEA	Retrofit	28,900	0.08

[a] 1964-65 base year

Operating Cost Data

In addition to the increased capital costs from including a NO_x reduction system in new or existing units, the increased unit operating costs may be considered. These differential operating costs were defined for 500 MW (electrical) new and existing units and are shown in Table 4-8 (Reference 4-31). The costs are given in 1975 dollars, and the equipment costs shown are determined from Figures 4-7a and b. To put these operating costs in perspective, they can be compared to the percent increase in generating costs shown at the bottom of Table 4-8. Except for the case of older units, the difference in operating cost is below 0.1 percent of annual cost.

Summary

Table 4-9 shows the impact on major system components, efficiency, and capacity when employing the major combustion modification NO_x control techniques. The relative changes in unit design or efficiency are shown to increase (or require addition) by a plus sign (+) or decrease by a minus sign (-). If the item is unchanged, or is altered to a negligible extent, it is indicated by a zero (0). Heat transfer surfaces remain unchanged in all cases (Reference 4-1).

The following are the major economic considerations that the boiler operator or designer may face:

- The lowest cost method for reducing NO_x emission levels on new and existing units is the incorporation of low excess air firing. Minimal additional costs are involved.
- For most utility boilers, the second lowest cost NO_x control method appears to be staged combustion by biased firing, "burners out of service" (BOOS) or addition of an overfire air system. Although lowering excess air (LEA) alone is less expensive than off-stoichiometric combustion, one utility company has found that when LEA is implemented concurrently with other control techniques, the excess air levels must be increased beyond those normally required.

TABLE 4-8. 1975 DIFFERENTIAL OPERATING COSTS OF OVERFIRE AIR ON NEW AND EXISTING TANGENTIAL, COAL-FIRED UTILITY BOILERS (Reference 4-31) (Net conversion efficiency = 0.359, March 1975 Equipment Costs)

	New Plant Without Overfire Air	New Plant With Overfire Air	Recent Existing With Added Overfire Air	Older Existing Without Overfire Air	Older Existing With Added Overfire Air
Capital Costs $/kW	500.00	500.20	500.70	250.00	250.70
Annual Cap. Cost $	40,000,000[a]	40,016,000	40,056,000	20,000,000[b]	20,056,000
Annual Fuel Cost $	18,000,000[c]	18,000,000	18,000,000	9,000,000[d]	9,000,000
Labor & Maint.[e] $	8,100,000	8,100,000	8,100,000	8,100,000	8,100,000
Total Annual Cost[f] $	66,100,000	66,116,000	66,156,000	37,100,000	37,156,000
Electricity Cost[g] mills/kWh	24.481	24.487	24.502	13.741	13.762
Increase — %	---	0.024	0.086	---	0.153
Increase — mills/kWh[f]	---	0.006	0.021	---	0.021

Based on:
[a] Annual fixed charge rate of 16% x 500 $/kW x 500,000 kW
[b] 16% x 250 $/kW x 500,000 kW
[c] 0.664 $/GJ coal cost, 500 MW, $\eta = 0.359$
[d] 0.332 $/GJ coal cost, 500 MW, $\eta = 0.359$
[e] Labor and maintenance cost of 3.0 mills/kWh
[f] 5,400 h/yr at 500 MW
[g] Cost at plant bus bar; transmission and distribution not included

TABLE 4-9. IMPACT OF NO_X CONTROL TECHNIQUES ON MAJOR UTILITY BOILER COMPONENTS

System Component	New Unit Design					Existing Units				
	OFA[a]	Sec. FGR[b]	a+b	Prim. FGR[c]	Water Inj.[d]	OFA	Sec. FGR[b]	a+b	Prim. FGR[c]	Water Inj.[d]
Forced Draft Fan Size	+	0	+	+	0 or +	0 or +	0	0 or +	+	0
Secondary Air Ducts	0	+	+	0	0	0	+	+	0	0
Windbox Size	0	+	+	+	0	0 or +	+	+	+	0
FGR Fan	N/A[e]	+	+	+	N/A	N/A	+	+	+	N/A
FGR Ducts	N/A	+	+	+	N/A	N/A	+	+	+	N/A
Dust Collectors	0	0	0	0	0	0	0	0	0	0
Coal Pulverizers	0	0	0	0	0	0 or +	0	0 or +	0	0
Convective Surface	0	+	+	+	+	N/A	N/A	N/A	N/A	N/A
Superheat Surface	0	-	-	-	-	N/A	N/A	N/A	N/A	N/A
Reheat Surface	-	-	-	-	-	N/A	N/A	N/A	N/A	N/A
Economizer Surface	0	+	+	+	+	N/A	N/A	N/A	N/A	N/A
Boiler Efficiency[f]	0	0	0	0	-	0	0	0	0	-
Capacity	0	0	0	0	0	0	-	-	-	-

[a] Overfire air system

[b] Flue gas recirculation through the secondary air duct and windbox compartments

[c] Flue gas recirculation to the transport air (primary air) of the coal pulverizers (mills)

[d] Water injection to the firing zone

[e] Not applicable

[f] Average heat rate, J/kWh

- Gas recirculation is significantly more costly to implement than overfire air and requires additional fan power. In existing units, the necessity to reduce unit capacity to maintain acceptable gas velocities through the boiler conventive sections may impose an additional penalty.
- For coal-fired units, gas recirculation to the coal pulverizers would cost approximately 15 percent less than windbox FGR; however, this may require increased excess air to maintain adequate combustion. In any case FGR is not particularly effective in reducing total NO_x emissions from coal-fired systems.
- Water injection involves moderate initial equipment costs, but due to high operating costs resulting from losses in unit efficiencies, it is the least desirable of the NO_x reduction techniques evaluated.
- In general, the cost of applying any of the control methods to an existing unit will be approximately two to three times that of a new unit design.
- Attention must be given to the base year in which control cost estimates were made. Figures on comparative electric power equipment costs from the most recent Marshall and Swift Equipment Cost Index (1974) indicate that such costs have increased 19 percent from 1972 and 16 percent from 1973. It is safe to assume that costs will be correspondingly higher in subsequent years.

4.1.2.2 Flue Gas Treatment

The flue gas treatment methods described in Section 3.2 included wet (oxidation followed by scrubbing) and dry (reduction) methods. Since most of these processes are still in the early stages of development, definite costs are, for the most part, not yet available. However, preliminary cost estimates have been made and are presented in Table 4-10. These estimates indicate that the capital and operating costs for some of these processes are comparable to existing flue gas desulfurization (FGD) systems.

4.1.3 Energy and Environmental Impact

In addition to affecting the cost of operating electrical generating combustion equipment, implementing NO_x control techniques can also impact overall plant efficiency and emissions levels of pollutants other than NO_x. These energy and environmental impacts are discussed below. The discussion emphasizes potential impacts due to applying combustion modification controls as these have been the most extensively studied and offer the greatest potential for widespread use in the

TABLE 4-10. COST ESTIMATES FOR COMBUSTION FLUE GAS TREATMENT PROCESSES

Process Type	Process	Application	Capital Cost	Operating Cost (mills/kWh)	Cost Base Year	Reference
Wet	Chiyoda Thoroughbred 102	Oil-fired boiler	\$80/kW[b]	3	1975	4-21
		Oil-fired boiler	\$100/kW[b]	4	1975	4-21
Wet	Sumitomo (Moretana)	Oil-fired boiler	\$60 to \$90/kW[b]	7	1973	4-21
Dry: selective catalytic reduction	Sumitomo	Gas-fired boiler	\$35/kW[b] or 40¢/Nm^3	1.2	1973	4-21
		Oil-fired boiler	\$80/kW[b]	nd[a]	1973	4-21
Dry: nonselective catalytic reduction	Sumitomo	Nitric Acid Plant	20¢/Nm^3	nd	1968	4-21
Dry: selective catalytic reduction	Hitachi	Oil-fired boiler	\$60/kW[b]	nd	1974	4-21
Dry: selective noncatalytic reduction (homogeneous decomposition)	Exxon	Coal-fired boiler	6¢ to 14¢/MJ	nd	1976	4-22

[a] nd = no data

[b] electrical output

near term. Due to a virtual lack of data, the potential effects of flue gas treatment techniques are only briefly mentioned. For the same reason, fuel switching and fuel additive effects are not treated at all.

4.1.3.1 Energy Impacts

The energy impacts of applying combustion modification NO_x controls to utility boilers occur largely through effects on unit fuel-to-steam efficiency. Although applying flue gas recirculation requires additional forced draft fan capacity, the additional energy penalties imposed to drive the fan are generally insignificant. Thus, effects on unit efficiency tend to dominate energy effects.

The efficiency effects of the combustion modifications for retrofit application are listed in Table 4-11. As the table shows, applying low excess air firing results in unit efficiency gains. For this reason the technique is gaining acceptance and becoming more a standard operating procedure than a specific NO_x control method in both old and new units.

The other commonly applied combustion modifications, FGR and off-stoichiometric firing, generally have little energy impact on utility boiler operation. In certain instances, higher overall excess air levels are required when using these techniques (especially for coal-firing) to prevent combustible losses. However, adverse effects are generally small.

A special point of concern relates to taking burners out of service on coal-fired boilers. Since, in a typical installation, each coal mill supplies a given set (generally a row or an elevation) of burners, applying BOOS generally involves removing a mill from service. However, the remaining mill capacity is usually insufficient to allow overfiring the remaining burners to maintain rated load. Thus implementing BOOS in a coal-fired unit may require derating the unit 10 to 20 percent. Of course, such derating represents a capacity loss, not an efficiency loss. But it is an energy related adverse impact nonetheless.

The remaining combustion modification techniques listed in Table 4-11, water injection and reduced air preheat, can impose quite significant energy penalties on utility boiler operation. As a consequence, these techniques are quite unpopular, and have found little acceptance.

Table 4-11 applies only to retrofit application of the common NO_x combustion controls. These same combustion modifications (LEA, FGR, off-stoichiometric combustion), in addition to low-NO_x burners, almost never adversely affect unit efficiency when designed in as part of a new unit. This illustrates that with suitable care during engineering and development, combustion modification NO_x controls can be incorporated into new unit designs with no adverse energy impacts.

TABLE 4-11. EFFECTS OF RETROFIT COMBUSTION MODIFICATION NO_x CONTROLS ON UTILITY BOILER EFFICIENCY (Reference 4-34)

Control	Effect on Efficiency	Comment
Low Excess Air	Up to 1.5% increase	Reduced stack gas heat loss
Flue Gas Recirculation	Insignificant	Small increase due to fan requirement
Off-Stoichiometric Combustion	Little effect with oil/gas firing Possible 1% decrease with coal firing	Possible increase in overall excess air needed for earlier burnout
Water Injection	About 10% decrease	Heat of vaporization of injected water lost
Reduced Air Preheat	About 1% efficiency loss per 30K decrease in air preheat temperatures	Increased stack gas heat loss

The situation with flue gas treatment is likely to be different; however, data are insufficient to allow any quantitative assessment of the potential penalties. For the case of oxidation/absorption wet processes it has been estimated that generation of the oxidizing agent (ozone) will require approximately 10 percent of the power plant electrical output (Reference 4-35). When this is added to the reheat requirements associated with all flue gas wet scrubbers, energy impacts may be quite significant.

4.1.3.2 Environmental Impact

Modification of the combustion process in utility boilers for NO_x control reduces the ambient levels of NO_2, which is both a toxic substance and a precursor for nitrate aerosols, nitrosamines, and photochemical smog. These modifications can also cause changes in emissions of other combustion generated pollutants. If unchecked, these changes, referred to here as incremental emissions, may have an adverse effect on the environment, in addition to effects on overall system performance. However, since the incremental emissions are sensitive to the same combustion conditions as NO_x, they may, with proper engineering, also be held to acceptable levels during control development so that the net environmental benefit is maximized. In fact, control of incremental emissions of carbon monoxide, hydrocarbons and particulate has been a key part of all past NO_x control development programs. In addition, recent control development has been giving increased attention to other potential pollutants such as sulfates, organics, and trace metals.

This section presents data obtained to date on the demonstrated effects of combustion modification NO_x controls on incremental emissions from utility boilers. Attention is focused on flue gas emissions as no data exist on incremental effects on liquid and solid effluents. Emphasis is placed on incremental CO, vapor phase hydrocarbon, and particulate emissions; although incremental sulfate and condensed phase organic emissions are briefly discussed. Lack of data precludes any discussion on the incremental effects of flue gas treatment, fuel switching, or fuel additive approaches to NO_x control.

Carbon Monoxide Emissions

Since large quantities of CO in the flue gas of utility boilers mean decreased efficiency, these boilers are operated to keep CO emissions at a minimum. Furthermore, if flue gas CO levels reach concentrations in excess of 2,000 ppm, severe equipment damage can result from explosions in flue gas exit passages. Thus, the degree to which a NO_x reduction technique is allowed to increase CO is limited by other than environmental concerns. In general, a NO_x control method is applied until flue gas CO reaches about 200 ppm. Further application is then curtailed.

NO_x control effects on CO emissions are highly dependent on the equipment type and the fuel fired. In utility boilers of newer design, it is generally possible to achieve good NO_x reduction without causing significant CO production. This is possible because newer burner and furnace designs allow for better combustion air control and longer combustion gas residence time. In addition, oil and coal-fired boilers usually emit very low CO levels during low NO_x combustion because smoke and soot production generally occurs with these fuels before significant CO levels are attained. Since boiler operators strive to keep combustible losses to a minimum, conditions which result in soot formation are avoided, resulting in correspondingly low CO levels. A summary of the field data on the effects of the more extensively implemented modifications on CO emissions are shown in Table 4-12. These data are discussed below for each combustion NO_x control.

As the data in Table 4-12 illustrate, lower excess air levels in utility boilers can have profound effects on CO emissions. In virtually all instances CO emissions increased significantly when excess O_2 levels were reduced 30 to 60 percent. Gas-fired boilers showed emission increases up to 400 percent when excess O_2 was lowered over this range, while oil-fired boilers were less sensitive, and showed CO emission increases from 0 to 120 percent. However, coal-fired boilers were the most sensitive to excess air reductions. Reducing excess O_2 by 40 to 60 percent gave 100 to 1,000 percent increases in CO emissions.

TABLE 4-12. REPRESENTATIVE EFFECTS OF NO$_x$ CONTROLS ON CO EMISSIONS FROM UTILITY BOILERS (References 4-12, 4-16, 4-19)

NO$_x$ Control	Fuel	CO Emissions (ppm)[a]	
		Baseline	NO$_x$ Control
Low Excess Air	Natural Gas	14	68
		86	74
		12	61
		8	8
		14	34
	Oil	19	42
		85	53
		15	20
		19	19
	Coal	42	93
		20	60
		24	283
		27	81
		27	225
Staged Combustion	Natural Gas	14	16
		86	67
		12	13
		14	14
	Oil	19	21
		85	85
		15	21
		28	37
	Coal	24	20
		27	26
		17	40
		31	45
Flue Gas Recirculation	Natural Gas	175	65
	Oil	21	9

[a] 3% O_2, dry basis.

Off-stoichiometric, or staged combustion has proven to be a very effective NO_x reduction technique for large steam generators. It can be implemented in a variety of ways including burners out of service, overfire air ports, and biased firing. In all cases, the effectiveness of staged combustion in reducing NO_x emissions depends in large part on the fraction of total combustion air that can be introduced into the second combustion stage. It is in this second stage that complete combustion of the fuel is achieved. CO emissions arise when this second stage combustion does not go to completion prior to quenching in the convective section. This is caused by a combination of the first stage being too fuel rich and the mixing of second stage air being too slow for the residence time provided. During development of retrofit or new design controls, these parameters are usually selected so that CO emissions are acceptable.

The effectiveness of staged combustion in reducing NO_x formation while keeping CO emissions low is highly dependent on specific equipment type. New utility boilers with multiburner furnaces are especially amenable to this technique because it is generally not difficult to adequately distribute secondary air and assure complete combustion in these sources. Consequently, implementing staged combustion in utility boilers is expected to elicit little effect on incremental CO emissions. This conclusion is certainly borne out by the representative data presented in Table 4-12.

The use of flue gas recirculation (FGR) for NO_x control has, in practice, been restricted to gas- and oil-fired units. This technique is ineffective in reducing fuel NO_x production, the predominant source of NO_x in coal firing. When FGR is implemented, 10 to 30 percent of the total burner gas flow is recycled flue gas from the boiler exhaust. Further FGR increases can cause flame instability due to reduced flame temperatures and oxygen availability. Theoretically, FGR can lead to increased CO emissions, but unacceptable flame instabilities usually occur before the onset of CO or smoke production. Thus, as Table 4-12 shows, the use of FGR has not caused increased CO emissions. On the contrary, CO emissions have generally decreased.

Hydrocarbon Emissions

Field test programs studying the effectiveness of NO_x controls often monitor flue gas HC emissions as a supplementary measure of boiler efficiency. Therefore, some data on the effect of these controls on HC emissions are available. Two recent test programs on utility boilers routinely measured flue gas HC (Reference 4-12 and 4-16). However, in virtually all tests, both baseline and low NO_x emissions were less than 1 ppm (or below the detection limit of the available monitoring instrument). Thus, it was concluded that HC emissions are relatively unaffected by imposing preferred NO_x combustion controls on large utility boilers. However, this conclusion is not altogether unexpected. The presence of unburned HC in flue gases implies poor boiler operating efficiency, and NO_x controls which significantly decrease efficiency have found little acceptance.

Particulate Emissions

Although gas-fired units produce negligible amounts of particulate, oil- and coal-fired utility boilers currently emit approximately 38 percent of the nationwide particulate and smoke (Reference 4-34). Potential adverse effects on these particulate emissions from NO_x combustion controls could therefore have significant environmental impact. Unfortunately the optimum conditions for reducing particulate formation (intense, high temperature flames as produced by high turbulence and rapid fuel/air mixing), are not the conditions for suppressing NO_x formation. Therefore, most attempts to produce low NO_x combustion designs have been compromised by the need to limit formation of particulates. This compromise has generally produced designs which maintain a well controlled, cool flame, while still providing sufficient gas residence time to completely burn carbon containing particles.

The NO_x combustion controls currently receiving the most widespread application in utility boilers are low excess air, off stoichiometric combustion, and flue gas recirculation (for gas and oil). The altered combustion conditions resulting from these modifications can be expected to influence emitted particulate load and size distribution. For example, smoke and particulate emissions tend to increase as available oxygen is reduced (soot emissions increase and ash particles contain more carbon). Thus the degree to which excess air can be lowered to control NO_x is usually limited by the appearance of smoke, especially in oil-fired units. Of course, the extent to which excess air can be limited depends on equipment types and design. Many modern burners can operate on as little as 3 to 5 percent excess air.

Similarly, the degree to which staged combustion can be employed is frequently limited by the degree to which the primary flame zone can be stably operated fuel-rich, how well the second stage air mixes with primary stage combustion products, and the residence time for combustion in the second stage. Soot and carbon particles formed in the fuel-rich primary stage tend to resist complete combustion downstream of that stage.

On the other hand, flue gas recirculation on oil-fired units can serve to decrease particulate emissions by providing more intimate mixing. Kamo, et al. (Reference 4-36) have demonstrated that recirculation rates of 40 to 50 percent on a heater-sized oil-fired furnace reduced the smoke number significantly.

Published data on the effects of NO_x reduction techniques on particulate emissions from utility boilers are scattered and insufficient for indepth analysis. Table 4-13 summarizes the particulate emissions data obtained during two recent field test programs which studied coal-fired utility boilers (References 4-12 and 4-16). During the studies, particulate measurments were recorded under baseline and low NO_x conditions. Since these NO_x conditions were generally produced by a combination of low excess air and staged combustion, the individual effect of each technique on particulate emissions cannot be determined. Nevertheless, the data do show that particulate emissions are relatively unaffected by low NO_x firing in front wall- and horizontally opposed-fired boilers. Tangentially-fired boilers, on the other hand, exhibit slightly increased particulate emissions under low NO_x conditions.

The effects of low NO_x firing on carbon (or combustible) content of the particulate are also shown in Table 4-13. Although the data are quite scattered, it appears that carbon losses increase for front wall- and horizontally opposed-firing under low NO_x conditions, but decrease slightly for tangential firing. However, the changes are small and may not be significant.

The effects of low NO_x conditions on emitted particle size distribution have also been investigated to a limited extent (Reference 4-12). The data from a study of particle size distribution in three boilers are summarized in Table 4-14. As the table shows, no significant changes were noted in two of the boilers, both of which were tangentially fired. In the third, a horizontally opposed boiler, a distinct shift to smaller particles was noted, but the author reported problems with the sampling and particle sizing equipment in this test, so the data may not be significant.

Sulfate Emissions

Ambient sulfate levels have recently become a matter of increasing concern in regions with large numbers of combustion sources, notably boilers, firing sulfur-bearing coal and oil. Although the direct health effects of high ambient sulfate levels are currently unclear (References 4-37 and 4-38), recent thought suggests that sulfates may be more hazardous than SO_2. For this reason, control of primary sulfate emissions is becoming a concern even though primary sulfates (directly emitted) comprise only 5 to 20 percent of ambient sulfate on a regional basis (Reference 4-38).

Since approximately 98 percent of the sulfur introduced into a utility boiler appears in flue gas as an oxide, applying NO_x controls would have essentially no effect on total SO_x emissions. However, effects on the emitted (SO_3 + particulate sulfate)/SO_2 ratio can be significant. Specifically, combustion conditions which limit local oxygen concentrations would be expected to decrease the

TABLE 4-13. EFFECTS OF NO_x CONTROLS ON PARTICULATE EMISSIONS FROM COAL-FIRED UTILITY BOILERS (References 4-12, 4-16)[a]

Firing Mode	Particulate Emissions (µg/J)		% Carbon on Particulate	
	Baseline	Low NO_x	Baseline	Low NO_x
Front-Wall	2.00 - 3.39	1.65 - 2.42	5.90 - 6.29	8.46 - 12.4
Horizontally Opposed	1.30 - 1.65	1.34 - 1.78	2.8 - 5.5	6.73 - 11.82
	3.29 - 3.83	2.40 - 3.60	0.53 - 0.69	0.18 - 0.46
Tangential	0.86 - 2.21	2.36 - 2.40	24.2 -25.8	14.8 - 18.8
	1.08 - 1.84	1.23 - 2.95	0.92- 1.98	0.8 - 1.53

[a] This table is included in Appendix A in English units.

TABLE 4-14. EFFECTS OF NO_x CONTROLS ON EMITTED PARTICLE SIZE DISTRIBUTION FROM COAL-FIRED UTILITY BOILERS
(Reference 4-12)

Equipment Type: Firing Mode	Firing Condition	Average Weight Percent Particles of Size:					
		>2.5 µm	2.0 µm	1.5 µm	1.0 µm	0.5 µm	<0.5 µm
Tangential	Baseline	81.78	9.12	2.01	2.64	2.92	1.55
	Low NO_x	80.74	8.91	2.28	2.92	3.25	1.88
Tangential	Baseline	92.75	2.97	0.70	0.97	1.21	1.38
	Low NO_x	93.94	1.89	0.59	0.86	1.10	1.61
Horizontally Opposed	Baseline	92.56	2.59	0.62	0.96	1.45	1.84
	Low NO_x	59.37	10.77	4.08	5.89	9.55	10.36

extent of SO_2 to SO_3 oxidation. Thus applying low excess air firing and off-stoichiometric combustion to control NO_x should also lower SO_3/sulfate emissions.

Confirming data, though sparse, do exist. Recent measurements have demonstrated the expected dependence of sulfate emissions on boiler excess air levels. Bennett and Knapp (Reference 4-39) have shown that particulate sulfate emissions increase with increasing boiler excess O_2 in oil-fired power plants. Homolya, et al. (Reference 4-40) report a similar increase in sulfate emissions as a percentage of total sulfur emissions with increasing excess O_2 in coal-fired boilers. Their data, shown in Figure 4-8, show a linear relationship between the sulfate fraction of emitted sulfur and boiler excess O_2. Other data (Reference 4-41), shown in Table 4-15, also show that SO_3 emissions decrease when staged combustion is used to control NO_x.

Organic Emissions

The term organic emissions as used here is defined to mean those organic compounds which exist as a condensed phase at ambient temperature. Thus they are organics which are either emitted as "carbon on particulate" or condense onto emitted particulate in the near-plume of a stack gas. These compounds, with few exceptions, can be classified into a group known variously as polycyclic organic matter (POM) or polynuclear aromatic hydrocarbons (PNA).

POM production is generally only a minor concern in gas-fired systems, of some concern in oil-fired sources, and of greater concern in coal-fired equipment. Like CO and HC emissions, POM emissions are the result of incomplete combustion. Since NO_x combustion controls can lead to inefficient combustion, if not carefully applied (especially low excess air and off-stoichiometric combustion), applying these controls can potentially lead to increased POM production.

Supporting data, however, are very limited, largely because of the difficulty of sampling flue gas streams for POM and of accurately assaying samples for individual POM species. Thompson et al., recently reported the effects of staged combustion and flue gas recirculation on POM emissions from a coal-fired utility boiler (Reference 4-13). Their data, shown in Table 4-16, seem to indicate that POM emissions do increase with two-stage combustion. However, they state that the sampling and laboratory analysis procedures used in obtaining the data varied over the sample set. Thus, they conclude that POM emissions are not significantly affected by firing mode. In another study, Bennett and Knapp (Reference 4-39) attempted to investigate the effects of boiler excess O_2 on POM emissions from an oil-fired utility boiler. They found that particulate carbon content increased with decreasing excess O_2. However, because POM assay data varied widely, even for baseline condition analyses, no conclusion regarding POM emissions was possible.

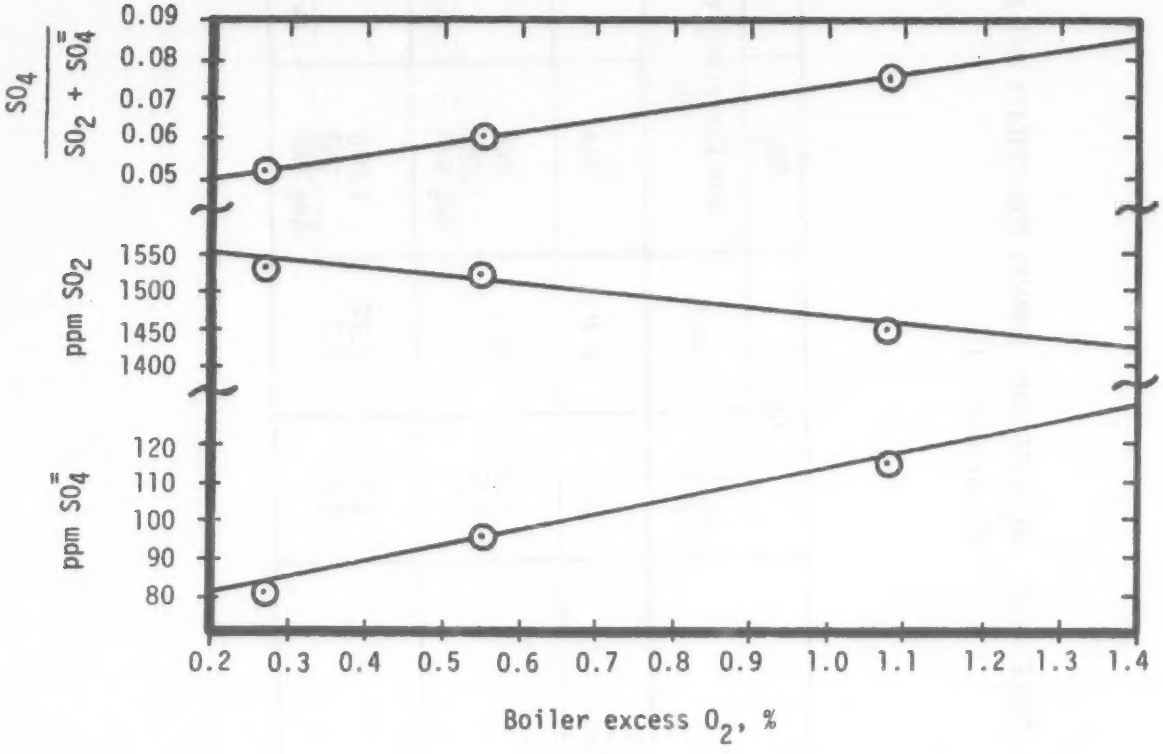

Figure 4-8. SO_2 conversion vs. excess oxygen in coal-fired utility boilers (Reference 4-40).

TABLE 4-15. SO_X EMISSIONS SUMMARY FOR UTILITY BOILERS
(Reference 4-41)

	O_2 (%)		SO_2	SO_3
	Boiler Exit	Stack	ppm Corrected to 3% O_2	
Baseline	2.9	6.8	944	28
LEA	1.55 1.5	5.7	948 1,000 Avg 974	13.5 35.9 Avg 25
OSC	3.1 3.4	7.72 7.1	1,010 968 Avg 989	14.0 13.9 Avg 14

TABLE 4-16. SUMMARY OF POM EMISSION TESTS FOR A COAL-FIRED UTILITY BOILER (Reference 4-13)

	Baseline (μg/m³)ᵃ	2-Stage Combustion (μg/m³)ᵃ	15% Gas Recirculation (μg/m³)ᵃ	2-Stage + 15% Recirculation (μg/m³)ᵃ
Anthracene/Phenanthrene	178.4	179.3	145.3	230.4
Methyl Anthracenes	53.4	48.5	89.4	98.3
Fluoranthene	51.5	110.3	24.7	43.7
Pyrene	15.1	52.1	23.3	46.9
Chrysene/Benz (A) Anthracene	0.3	--	--	--
Total POM	298.7	390.2	282.7	419.3
(Percent of Baseline)	(100)	(131)	(95)	(140)

[a] 3% O_2, dry basis.

4.2 INDUSTRIAL BOILERS

Industrial boilers range in capacity from 3 to 73 MW*, (10 to 250 million Btu/hr), and comprise a wide diversity of firing types and fuels. In 1974, industrial boilers consumed about 30 percent of the fossil fuel used by stationary sources. The industrial boiler capacity distribution was approximately 49 percent gas-fired, 29 percent oil-fired and 22 percent coal-fired. About a third of the industrial units are small packaged boilers. Fifty-three percent are in the 5 to 30 MW (17 to 100 x 10^6 Btu/hr) range and are primarily packaged watertube units. A more complete description of this equipment category is given in Section 2.3.2.

NO_x emissions from industrial-size boilers amounted to 2.2 Tg per year (2.44 x 10^6 tons) in 1974, or 18.2 percent of the nationwide stationary source emissions.

The following discussion of NO_x control techniques centers on the most promising method, combustion modifications.

4.2.1 Control Techniques

The data on applied combustion modification technology for industrial boilers are limited. The most extensive results were derived from a recent EPA-sponsored study (Reference 4-49, 4-50). This study involved the field testing of a representative sample of industrial boilers to determine their NO_x reduction potential. Ten different combustion modification techniques were implemented.

The effects of these techniques on NO_x emissions and boiler efficiency are summarized in Figure 4-9 for 73 separate boiler tests. The ten techniques are listed at the top of the figure. The graph is divided into quadrants. The criterion for the best quadrant is that the modification technique should simultaneously reduce NO_x and increase efficiency. In general, the study showed that total NO_x emission reductions of up to 47 percent were possible by using one or a combination of six different methods. These were: excess air reduction, burner-out-of-service (BOOS), flue gas recirculation (FGR), overfire air addition, burner register adjustment, and reduced air preheat. Only with the first three methods was boiler efficiency generally unimpaired.

Of these three, lowering excess air was the preferred method because boiler efficiency was usually maintained or improved, and particulate emissions did not increase, as they do with most of the other techniques. FGR is the next most promising technique, since particulate emissions

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*Approximately 1 percent of the industrial boilers are greater than the 73 MW (250 x 10^6 Btu/hr) classification for which new source performance standards have been established (Reference 4-42). These boilers are essentially the same as utility boilers.

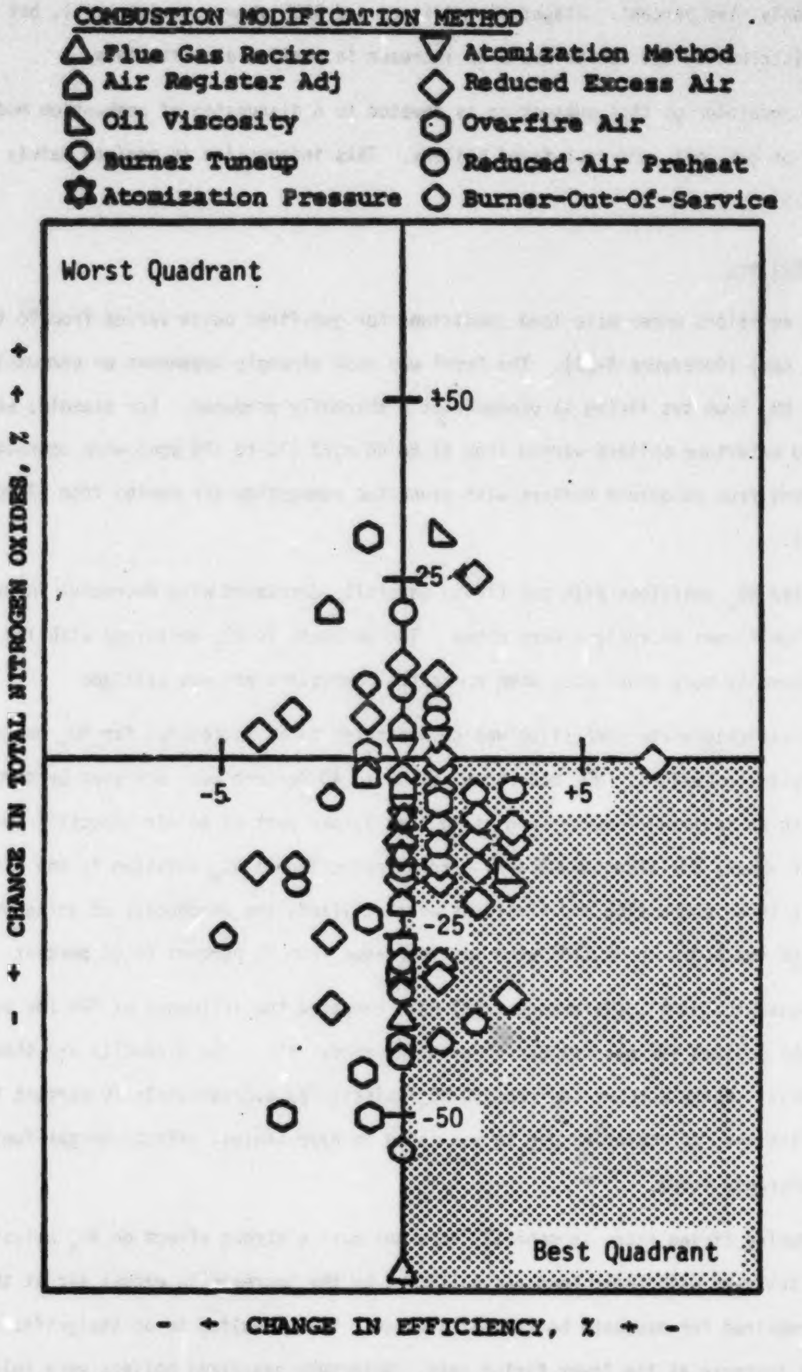

Figure 4-9. Effect of combustion modification methods on total nitrogen oxides emissions and boiler efficiency (Reference 4-50).

increased only five percent. Staged air addition and BOOS show some potential, but difficulties exist in distributing the air to avoid an increase in particulate emissions.

The remainder of this subsection is devoted to a discussion of combustion modification experience on gas, oil, and coal-fired boilers. This information is derived mainly from References 4-49 and 4-50.

Gas-Fired Boilers

NO_x emissions under base load conditions for gas-fired units varied from 26 to 190 ng/J (50 to 375 ppm) (Reference 4-51). The level was most strongly dependent on combustion air temperature since NO_x from gas firing is predominantly thermally produced. For example, emissions from base loaded watertube boilers varied from 37 to 60 ng/J (70 to 116 ppm) when operated on ambient air. NO_x emissions from watertube boilers with preheated combustion air varied from 47 to 190 ng/J (90 to 375 ppm).

Boiler NO_x emissions with gas firing generally decreased with decreases in excess air level although significant exceptions were noted. The decrease in NO_x emissions with low excess air firing was generally more pronounced when preheated combustion air was utilized.

Off-stoichiometric combustion was demonstrated to be successful for NO_x control in multi-burner, gas-fired boilers. NO_x reductions of 12 to 40 percent were achieved by terminating the fuel flow to an individual burner and using that burner port as an air injection port. Simultaneous limiting of excess air also showed a 24 percent reduction in NO_x emission in one instance. In the tests where these combustion modifications were utilized, the percentage of units with emissions less than 86 ng/J (0.2 lb $NO_2/10^6$ Btu) was increased from 75 percent to 82 percent.

Cichanowicz et al. (Reference 4-52) have compared the influence of FGR for both watertube and firetube boilers for natural gas at constant excess air. These results are shown in Figures 4-10 and 4-11. Forty percent FGR reduced NO_x emission by approximately 70 percent for both these boilers. Flue gas recirculation *per se* was found to have minimal effects on gas fueled boiler efficiency (Reference 4-50).

Reducing firing rate, in general, does not have a strong effect on NO_x emissions. The NO_x reduction achieved with lower load was nullified by the increase in excess air at the reduced load that was required for adequate boiler performance. This resulted in an insignificant NO_x decrease or even an increase at the lower firing rate. Watertube gas-fired boilers were relatively insensitive to load changes unless they were equipped with preheaters. In this case, NO_x reductions of

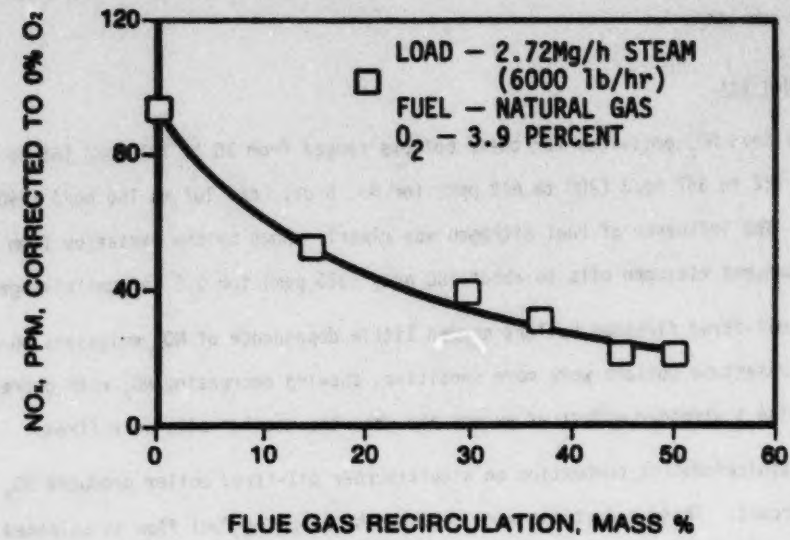

Figure 4-10. The influence of flue gas recirculation on NO_x emissions from a firetube boiler (Reference 4-52).

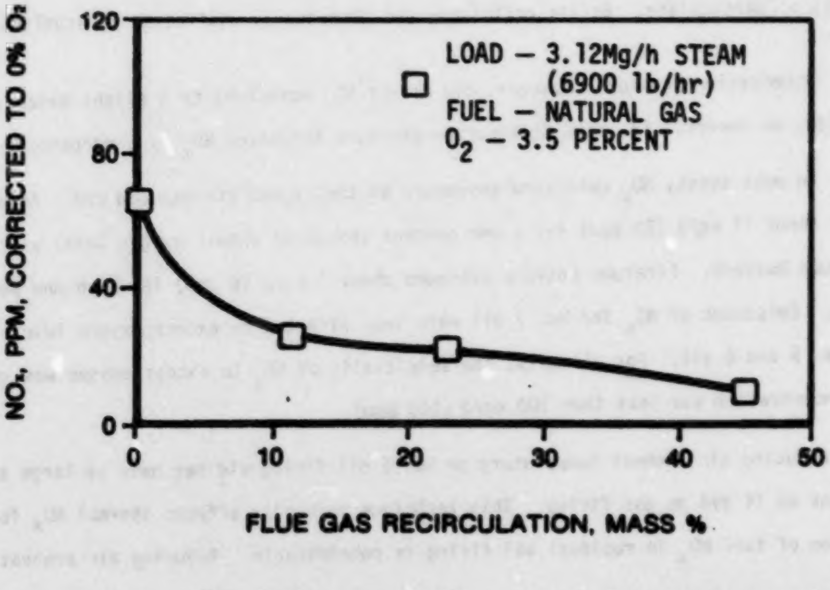

Figure 4-11. The influence of flue gas recirculation on NO_x emissions from a watertube boiler (Reference 4-52).

about 20 percent were obtained as the firing rate was dropped from 100 percent to 50 percent of name plate capacity.

Oil-Fired Boilers

Base load NO_x emissions for these boilers ranged from 36 to 101 ng/J (65 to 180 ppm) with No. 2 oil, 112 to 347 ng/J (200 to 619 ppm) for No. 5 oil, and 107 to 196 ng/J (190 to 350 ppm) for No. 6 oil. The influence of fuel nitrogen was clearly shown by the variation from 50 ng/J (90 ppm) for 0.045 percent nitrogen oils to about 180 ng/J (325 ppm) for 0.5 percent nitrogen fuel oils.

The oil-fired firetube boilers showed little dependence of NO_x emissions on excess air or load. The watertube boilers were more sensitive, showing decreasing NO_x with decreased excess air. There was also a stronger effect of excess air when the heavier oils were fired.

Off-stoichiometric combustion on a multiburner oil-fired boiler produced NO_x reductions of 17 to 49 percent. These reductions were achieved by stopping fuel flow to selected burners and using the burner port as an air injection port. It was also shown that using upper burners as air injection ports gave better results than using lower burners. This is not a general recommendation, because this kind of result is highly dependent on the individual internal flow patterns of a particular boiler.

Emissions of NO_x were found to be relatively independent of the fuel oil atomization method, but dependent on the characteristics of the individual burner. For a given oil burner, the atomization method that produced the lowest nitrogen oxide emissions also generally produced the greatest quantity of particulate. Boiler efficiency was essentially unaffected by atomization method.

Atomization pressure, however, did effect NO_x emissions to a slight extent. In one series of tests, an increase in steam atomization pressure increased NO_x by 6 percent.

In most tests, NO_x emissions decreased as the excess air was reduced. An average change in NO_x of about 11 ng/J (20 ppm) for a one percent change of excess oxygen level was observed for watertube boilers. Firetube boilers averaged about 3 ng/J (6 ppm) for each one percent change in oxygen. Emissions of NO_x for No. 2 oil were less affected by excess oxygen level than were those for Nos. 5 and 6 oil. For all oils, the sensitivity of NO_x to excess oxygen was small when the total NO_x concentration was less than 100 ng/J (180 ppm).

Reducing air preheat temperature on No. 6 oil firing did not have as large an effect on NO_x emissions as it did on gas firing. This technique primarily affects thermal NO_x formation; the contribution of fuel NO_x in residual oil firing is considerable. Reducing air preheat resulted in an efficiency decrease of about 2.5 percent per 50K increase in stack temperature. For general application, this technique would require an increase in economizer area to maintain overall efficiency.

Flue gas recirculation was implemented on a watertube boiler firing a No. 6 oil. At a minimum excess oxygen level of 2 percent, adding 20 percent FGR to a steam-atomized flame lowered NO_x by 50 percent. For an air-atomized burner, less dramatic NO_x reduction effects were experienced at both nominal and minimum excess oxygen levels. For oil firing in general, FGR rates greater than 27 percent caused flame instability and blowout.

The effect on NO_x emissions of tuning the burner was also determined. Tuning involved nozzle examination, spray angle adjustment, and flame length adjustment. The chief effect of burner modification was a reduction in carbon monoxide rather than NO_x. Particulate generally increased after tuneup. The most effective method of reducing NO_x by tuning was to reduce excess oxygen and accept some increase in CO emissions.

Coal-Fired Boilers

The baseline NO_x emissions from coal-fired boilers were generally higher than those from gas and oil-fired units. Emissions ranged from 100 to 550 ng/J (165 to 900 ppm). Although the fuel nitrogen contents of the test coals were high, ranging from 0.8 to 1.5 percent by weight, the field studies indicated no strong dependence of NO_x emissions upon fuel nitrogen content. Other factors are apparently more important in determining NO_x production, such as furnace geometry, excess air, firing rate, burner type, and other fuel properties.

It was found that pulverized and spreader stoker-type boilers produced the highest — 550 ng/J — baseline NO_x emissions. Chain grate and underfed stokers had the lowest — 100 ng/J — emissions. In these latter units, the combustion air fed up through the grating is insufficient for complete oxidation, so additional air must be introduced above the grating through overfire air ports. The combustion is, therefore, effectively staged, and the NO_x emissions were quite low (100 ng/J or 165 ppm).

Spreader stokers, in which the fuel is introduced with the air flow above the grate, had intermediate emission characteristics. Some of the fuel is burned in suspension, and the remainder is combusted on the grate as in the underfeed stoker. The resultant combustion is only partially staged. The combustion intensities are also higher than for underfed stokers, possibly increasing thermal NO_x formation.

The pulverized coal units, especially the cyclone-fired types, produced the highest baseline emissions due mainly to the very high combustion intensity.

Reducing excess oxygen in coal-fired boilers was found to be more effective in reducing NO_x than in either oil or gas-fired boilers. Each one percent change in excess oxygen resulted in approximately a 37 ng/J (60 ppm) change in NO_x emission, regardless of air preheat temperature. This strong, consistent, decrease in NO_x with decreasing excess air was unique to coal; the NO_x occasionally increased when excess oxygen was decreased on oil and gas firing. Also, the average amount of excess air fired for coal averaged 8.7 percent, which was significantly higher than for oil or gas.

The overfire air concept was tested on several stoker fired boilers, and the results were disappointing. The above-grate air injection ports (conventional equipment on all stokers) reduced NO_x by only 8 percent. It was concluded that the ports were located too far from the primary flame zone or that the overfire air system lacked the capacity to alter the air/fuel ratio sufficiently for NO_x reduction.

The effect of firing rate was investigated by varying the boiler load about the base load point of 80 percent of nameplate capacity. Generally, coal-fired watertube boilers showed an increase in NO_x when operating below 60 percent capacity. This increase usually coincided with an excess air increase.

Another EPA-sponsored study is assessing the potential of substituting western U.S. subbituminous coals for eastern bituminous coals as an industrial boiler fuel (Reference 4-53). The results of the program are significant from a NO_x control standpoint since switching to this more abundant coal may become widespread in the near future. The western coals were found to be compatible with the industrial boilers of current design, although two units of older design (underfed and traveling grate stokers) had some combustion difficulties. The coals were superior to eastern coals in terms of lower NO_x, SO_x, particulate, and unburned hydrocarbon emissions. In addition, they could be fired at lower excess air than eastern coal, and produced much lower combustible losses.

To summarize, it appears that significant NO_x emission reduction can be obtained in most industrial boilers with minor modifications in operating conditions. Additional emission reductions are possible with boiler redesign which would permit cost-effective implementation of off-stoichiometric or staged-combustion in units burning heavy fuel oils or coal. Very few existing units possess the necessary flexibility for this type of major retrofit. Problems which must be considered in the design of new units, and particularly in the modification of existing units, include corrosion and deposits on boiler tubes, flame instability, and combustion noise. The level of NO_x reduction that is achievable on industrial boilers is close to, but generally not as great as, that attainable with utility boilers. The Industrial Environmental Research Laboratory — RTP of the EPA is continuing to develop cost-effective NO_x reduction methods for industrial boilers.

4.2.2 Costs

Cost data for combustion modifications on industrial boilers are virtually nonexistent. Only the most broadly based estimates are available to the boiler owner and operator at the present time. The most recent information of this kind was published in Reference 4-50. In that industrial boiler field study, a 5.1 MW (17.5×10^3 lb steam/hr) D-type watertube boiler was modified by adding staged air and flue gas recirculation capability. The windbox depth was increased and a second set of registers to control the recirculating flue gas was installed inside the extension. The cost of these modifications was estimated at $5000. (The current cost of new boilers of this type is about $60,000.) The cost of a similar modification on other modern D-type boilers could be as high as $7500 if the existing burner registers cannot be used.

Manufacturers of industrial boilers in the 90 MW (300×10^3 lb steam/hr) size range and one million dollar cost category estimated that a staged air installation in general would add 2 to 4 percent to the boiler's cost. Specifically for A-type boilers, the incremental cost would be about 2 percent, and for D-type about 3 percent. Another booster air fan, if required, would increase the modification cost by about one percent (Reference 4-50).

In a recent study, costs for retrofitting an existing unit to accept flue gas recirculation were estimated (Reference 4-54). Approximate costs, which include design, installation and equipment costs associated with the retrofit of FGR systems were, in 1975 dollars, $20,340 for a 3.51 MW firetube boiler and $21,190 for a 3.51 MW watertube boiler. However, these costs would be considerably less for a new boiler. Reference 4-54 estimates that for a new boiler of the size mentioned above, the cost of including an FGR system will be about $6,900.

Research and development, including field testing and application of NO_x control methods to this equipment category, is still in its early stages. More accurate cost estimates for these techniques are being developed as part of ongoing and planned EPA studies.

4.2.3 Energy and Environmental Impact

As was the case for utility boilers, the energy impacts of applying combustion modification NO_x controls to industrial boilers occur almost exclusively through effects on boiler efficiency. Data on these efficiency effects of NO_x control from the most extensive field study of industrial boilers to date (References 4-49 and 4-50) were presented in Figure 4-9. As the figure indicated, only with low-excess air, BOOS, and FGR was boiler efficiency generally unimpaired. For low excess air firing, efficiency gains of from 1 to 3 percent were typical. Taking burners out of service and FGR generally did not affect efficiency. On the other hand, other tested controls generally imposed efficiency penalties. Both overfire air and reduced air preheat gave efficiency losses of 1 to 2 percent.

The effects of NO_x combustion modification controls on incremental pollutant emissions from industrial boilers should also be analogous to those described previously in Section 4.1.3.2 for utility boilers. Unfortunately, the only currently circulated data are on incremental flue gas CO, HC, and particulate effects.

Carbon Monoxide Emissions

The bulk of the data on incremental CO emissions due to NO_x controls applied to industrial boilers was obtained in the two previously cited field test programs (Reference 4-49 and 4-50). In these studies, CO emissions were reported for both baseline and for low NO_x firing. Baseline emissions were recorded with the boiler operating at 80 percent of rated capacity under normal (or as-found) conditions. Low NO_x testing was implemented until CO emission levels reached 100 to 200 ppm, then it was curtailed.

The data obtained during these studies are summarized in Table 4-17. As indicated in the table, baseline CO emissions for industrial boilers are generally insignificant. However, the application of NO_x combustion controls in most cases adversely affected CO levels because each control was implemented until CO levels became unacceptable.

As noted for utility boilers, CO emissions from industrial boilers are also adversely affected by lowering excess air levels. As observed in the field study and shown in Table 4-17, CO emissions from gas- and oil-fired boilers can be significantly increased when excess oxygen is reduced 20 to 50 percent. Coal-fired boilers showed lower residual CO emission increases.

Two methods were used in the industrial boiler study to effect staged combustion: overfire air and burners out of service. In these tests baseline CO emissions were always low. Combustion staging by both methods generally resulted in unchanged to slightly increased CO emissions.

The data in Table 4-17 show that FGR has little effect on CO emissions. This conclusion substantiates what was noted in the utility boiler testing discussed in Section 4.1.3.1. In addition, the data in Table 4-17 illustrate that varying combustion air temperature has almost no

TABLE 4-17. EFFECTS OF NO_x CONTROLS ON CO EMISSIONS FROM INDUSTRIAL BOILERS
(References 4-49 and 4-50)

NO_x Control	Fuel	CO Emissions (ppm)[a]	
		Baseline	NO_x Control
Low Excess Air	Natural Gas	10 0 0 0 50	10 0 11 900 129
	Distillate Oil	47 90 0	485 150 17
	Residual Oil	0 0 0 0 0	45 100 9 28 205
	Coal	25 70 0 0 25	20 60 0 22 25
Staged Combustion • Overfire Air	Natural Gas	10 10	10 20
	Distillate Oil	0	0
	Residual Oil	0 0 0	0 30 80
	Coal	0	49
• Burners Out of Service	Natural Gas	10 0 0	10 0 43
	Residual Oil	10 0 0	20 0 10
Flue Gas Recirculation	Natural Gas	10 10	0 75
	Residual Oil	0 0	0 0
Variable Air Preheat	Natural Gas	10 0 322	0 30 320
	Residual Oil	0 0	0 0
	Coal	0	10

[a] 3% O_2, dry basis.

effect on CO emissions. These observations suggest that effects of peak flame temperature on CO emissions were also insignificant.

Hydrocarbon Emissions

The field test program investigating NO_x controls applied to industrial boilers also reported data on incremental HC emissions. These data are summarized in Table 4-18 and show that the use of NO_x combustion controls generally do not affect flue gas HC levels. Some tests show a slight increase in HC emissions, yet others indicate slight reductions. Based on these data, it seems fair to conclude that HC emissions from boilers are unaffected when implementing NO_x combustion controls.

Particulate Emissions

In addition to the above data, the industrial boiler test program reported some particulate emissions and size distribution data showing the effects of several NO_x combustion controls. These particulate emissions data from several oil- and coal-fired boilers are summarized in Figure 4-12. The figure shows changes in particulate emissions versus changes in NO_x emissions from baseline conditions as a function of the applied NO_x control.

As Figure 4-12 shows, the effects of NO_x controls on particulate emissions are mixed. For example, both forms of staged combustion tested increased particulate emissions by 15 to 90 percent, while flue gas recirculation increased emissions by 10 percent. In contrast, reducing air preheat decreased particulate emissions by 45 percent. Furthermore, low excess air firing generally lowered particle emissions 25 to 60 percent.

These observations are in general agreement with those of Heap, et al. (Reference 4-54) who studied FGR and staged combustion applied to two oil-fired packaged boilers. They found that smoke emissions increased slightly when both FGR and staged combustion were applied.

Cato, et al. (Reference 4-50) also reported some very limited particle size distribution data, shown in Figure 4-13. This figure shows that, in a distillate oil-fired boiler, as excess air levels are lowered, the emitted particle size distribution shifts slightly to larger sizes. A more pronounced shift to larger particle sizes was observed with reduced load in a residual oil-fired boiler. However, these data are much too limited to allow any definite conclusions to be made regarding the effects of combustion modifications on flue gas particle size distribution.

TABLE 4-18. REPRESENTATIVE EFFECTS OF NO_x CONTROLS ON VAPOR PHASE HYDROCARBON EMISSIONS FROM INDUSTRIAL BOILERS (References 4-49 and 4-50)

NO_x Control	Fuel	HC Emissions (ppm)[a]	
		Baseline	NO_x Control
Low Excess Air	Natural Gas	42 10 17 7	34 0 13 8
	Distillate Oil	3	9
	Residual Oil	8 35	13 25
	Coal	11 21	18 7
Staged Combustion • Overfire Air	Natural Gas	5	0
	Distillate Oil	0	0
	Residual Oil	0	0
• Burners Out of Service	Natural Gas	0	0
	Residual Oil	12 35	14 15
Flue Gas Recirculation	Residual Oil	0	0
Variable Air Preheat	Natural Gas	10	0
	Residual Oil	15 35	13 25

[a] 3% O_2, dry basis.

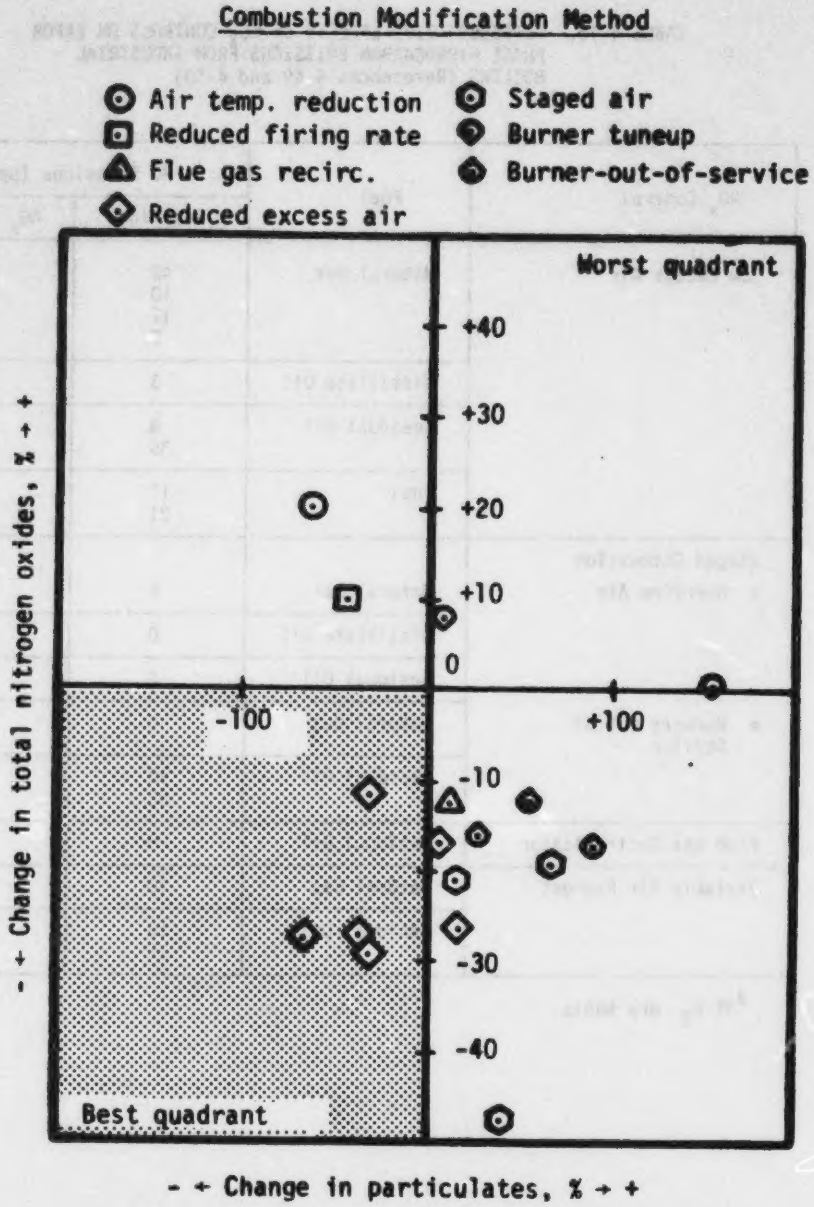

Figure 4-12. Effect of NO_x Controls on solid particulate emissions from industrial boilers (Reference 4-50).

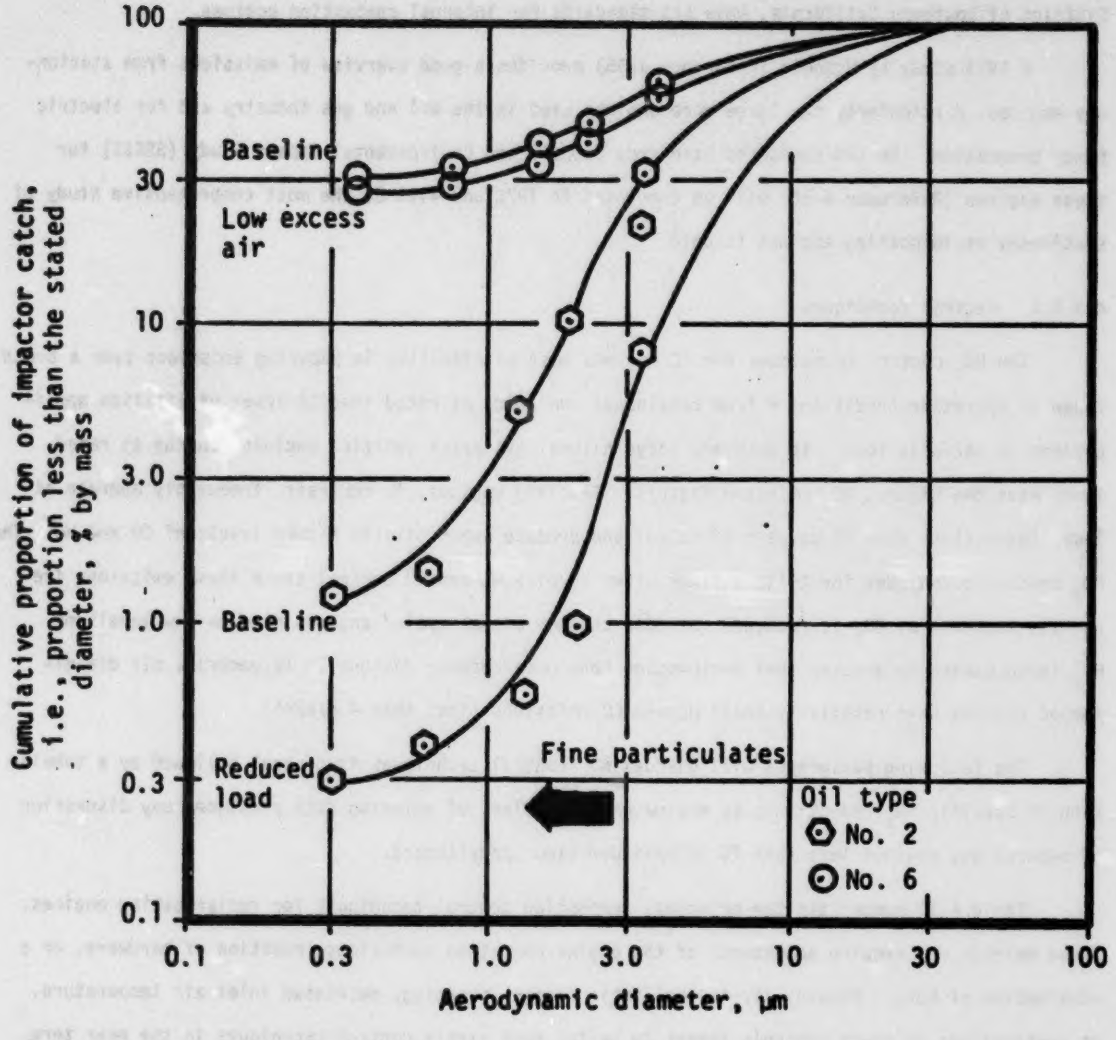

Figure 4-13. Effects of NO_x controls on particulate size distribution from oil-fired industrial boilers (Reference 4-50).

4.3 PRIME MOVERS

4.3.1 Reciprocating Internal Combustion Engines

Stationary reciprocating engines account for nearly 20 percent of the NO_x from stationary sources, or 2.4 Tg per year (2.66×10^6 tons). There are presently no Federal regulations for gaseous emissions from these engines. Some local areas, such as the South Coast Air Pollution Control District of Southern California, have set standards for internal combustion engines.

A 1973 study by McGowin (Reference 4-55) provides a good overview of emissions from stationary engines, particularly the large bore engines used in the oil and gas industry and for electric power generation. An EPA-sponsored Standards Support and Environmental Impact Study (SSEIS) for these engines (Reference 4-56) will be completed in 1978 and will be the most comprehensive study of stationary reciprocating engines to date.

4.3.1.1 Control Techniques

The NO_x control techniques for IC engines must be effective in reducing emissions over a broad range of operating conditions — from continuous operation at rated load to lower utilization applications at variable load. In general, large natural gas spark ignition engines running at rated loads have the highest NO_x emission factors. Gasoline engines, in contrast, frequently operate at lower loads (less than 50 percent of rated) and produce substantially higher levels of CO and HC. The NO_x control techniques for these engines often involve HC and CO control since these emissions frequently increase as NO_x is reduced. Divided chamber diesel-fueled engines produce low levels of NO_x (accompanied by greater fuel consumption than open chamber designs). In general, all diesel-fueled engines have relatively small HC and CO emissions (less than 4 g/kWh*).

The following paragraphs will discuss NO_x control techniques in general followed by a tabulation of specific NO_x reductions, by engine group. A lack of emission data precludes any discussion of natural gas engines less than 75 kW/cylinder (100 hp/cylinder).

Table 4-19 summarizes the principal combustion control techniques for reciprocating engines. These methods may require adjustment of the engine operating conditions, addition of hardware, or a combination of both. Retard, air-to-fuel ratio change, derating, decreased inlet air temperature, or combinations of these controls appear to be the most viable control techniques in the near term. Nevertheless, there is some uncertainty regarding maintenance and durability of these techniques because, in the absence of regulation, very little data exists for controlled engines outside of laboratory studies, particularly for large stationary engines. In general, increases in fuel consumption, as much as 10 percent, are the most immediate consequence of the application of these

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*shaft output

TABLE 4-19. SUMMARY OF NO_x EMISSION CONTROL TECHNIQUES FOR RECIPROCATING INTERNAL COMBUSTION ENGINES

CONTROL	PRINCIPLE OF REDUCTION	APPLICATION	BSFC[d] INCREASE	COMMENTS -- LIMITATIONS
RETARD Injection (CI)[a] Ignition (SI)[b]	Reduces peak temperature by delaying start of combustion during the combustion stroke.	An operational adjustment. Delay cam or injection pump timing (CI); delay ignition spark (SI).	Yes	Particularly effective with moderate amount of retard; further retard causes high exhaust temperature with possible valve damage and substantial BSFC increase with smaller NO_x reductions per successive degree of retard.
CHANGE AIR-TO-FUEL (A/F) RATIO	Peak combustion temperature is reduced by off-stoichiometric operation.	An operational adjustment. Increase or decrease to operate on off-stoichiometric mixture. Reset throttle or increase air rate.	Yes	Particularly effective on gas or dual-fuel engines. Lean A/F effective but limited by misfiring and poor load response. Rich A/F effective but substantial BSFC, HC, and CO increase. A/F less effective for diesel-fueled engines.
DERATE	Reduces cylinder pressures and temperatures.	An operational adjustment, limits maximum bmep[c] (governor setting).	Yes	Substantial increase in BSFC with additional units required to compensate for less power. HC and CO emission increase also.
INCREASE SPEED	Decreases residence time of gases at elevated temperature and pressure.	Operational adjustment or design change.	Yes	Practically equivalent to derating because bmep is lowered for given power requirements. Compressor applications constrained by vibration considerations. Not a feasible technique for existing and most new facilities.
DECREASE INLET MANIFOLD AIR TEMPERATURE	Reduces peak temperature.	Hardware addition to increase aftercooling or add aftercooling (larger heat exchanger, coolant pump).	No	Ambient temperatures limit maximum reduction. Raw water supply may be unavailable.
EXHAUST GAS RECIRCULATION (EGR) External	Dilution of incoming combustion charge with inert gases. Reduce excess oxygen and lower peak combustion temperature.	Hardware addition; plumbing to shunt exhaust to intake; cooling may be required to be effective; controls to vary rate with load.	No if EGR rates not excessive	Substantial fouling of heat exchanger and flow passages; anticipate increased maintenance. May cause fouling in turbocharged, aftercooled engine. Substantial increases in CO and smoke emissions. Maximum recirculation limited by smoke at near rated load, particularly for naturally aspirated engines.
Internal valve overlap or retard	Cooling by increased scavaging, richer trapped air-to-fuel ratio.	Operational hardware modification: adjustment of valve cam timing.	Yes	Not applicable on natural gas engine due to potential gas leakage during shutdown.
exhaust back pressure	Richer trapped air-to-fuel ratio.	Throttling exhaust flow.	Yes	Limited for turbocharged engines due to choking of turbocompressor.
CHAMBER MODIFICATION Precombustion (CI) Stratified charge (SI)	Combustion in antechamber permits lean combustion in main chamber (cylinder) with less available oxygen.	Hardware modification; requires different cylinder head.	Yes	5 to 10 percent increase in BSFC over open-chamber designs. Higher heat loss implies greater cooling capacity. Major design development.
WATER INDUCTION	Reduces peak combustion temperature.	Hardware addition: inject water into inlet manifold or cylinder directly; effective at water-to-fuel ratio = 1 (kg H_2O/kg fuel).	No	Deposit buildup (requiring demineralization); degradation of lube oil, cycling control problems.
CATALYTIC CONVERSION	Catalytic reduction of NO to N_2.	Hardware addition: catalytic converter installed in exhaust plumbing or reducing agent (e.g. ammonia) injected into exhaust stream.	No	Catalytic reduction of NO is difficult in oxygen-rich environment. Cost of catalyst or reducing agent high. Little research applied to large-bore IC engines.

[a] Compression ignition

[b] Spark ignition

[c] bmep -- brake mean effective pressure .

[d] BSFC -- brake specific fuel consumption

techniques (excluding inlet air cooling). All control techniques involve only operational adjustments with the exception of (1) derating which may require additional installed capacity to compensate for the decreased rating, (2) inlet manifold air cooling which involves the addition of a heat exchanger and a pump, and (3) catalytic conversion, which requires adding a catalytic reactor.

While exhaust gas recirculation (EGR) yields effective reduction of NO_x, this technique requires additional development to overcome fouling of flow passages and increased smoke levels. In general, recirculated exhaust is cooled in order to be effective. This practice promotes fouling. EGR has not been field tested for large engines, and has been rejected by one manufacturer of heavy-duty diesel truck engines and limited by another manufacturer. EGR has potential application in naturally aspirated engines if full load EGR cutoff is provided to prevent excessive smoke (<10 percent opacity). EGR, however, has been applied successfully in combination with other techniques, such as retard, in gasoline-fueled automobile engines (References 4-56, 4-57).

Water injection, similarly, has serious maintenance and durability problems associated with mineral deposit buildup and oil degradations. Despite use of demineralized water and increased oil changes, the control problems associated with engine startup and shutdown persist. This factor, coupled with the need for a water source, has led manufacturers to reject this technique (Reference 4-56).

Combustion chamber modifications such as precombustion and stratified chambers have demonstrated large NO_x reductions, but also produce substantial fuel consumption increases (5 to 8 percent more than open chamber designs). With the rapid increases in the price of diesel fuel and gasoline, manufacturers have been reluctant to implement this technique. In fact, one manufacturer of divided chamber engines is vigorously pursuing development of low emission open chamber engines (Reference 4-56).

Table 4-20 summarizes emission reductions achieved with large bore engines by use of retard, air/fuel ratio changes, derating, and reduced inlet manifold air temperature (MAT). This table includes only those techniques from Table 4-19 which could be readily applied by the user. The cited emission reductions are based on results obtained from engines tested in manufacturers' laboratories. Therefore, some uncertainty exists concerning durability and maintenance over longer periods of operation. In general, the greatest NO_x reductions are accompanied by the larger increases in fuel consumption. This is a direct result of reducing peak combustion temperatures and, thus, decreasing thermal efficiency.

TABLE 4-20. EFFECT OF NO_x CONTROLS ON LARGE-BORE INTERNAL COMBUSTION ENGINES

a. Normalized percent reductions of NO_x

Fuel	Gas				Dual Fuel		Diesel		
Number Cylinders	2		4		2	4	2		4
	BS[b]	TC	NA	TC	TC	TC	BS	TC	TC
Baseline[a]	20	17	24-29	17-30	12	10-17	18-26	14-19	13-15
Retard	2.5	3.1	1.5	4.1-0.6	9.1	1.5-6-3	6.9	5.3-5.7	2.7-4.4
Air-to-Fuel	0.19	4.5	1.8	3.3	1.7	2.4-2.5	—	—	
Derate	6.2	2.6	0.25-1.3	0.34-1.9	—	0.01-0.94	0.84-0.92	—	0.17
MAT	0.9	1.3	—	0.4-0.9	1.3	0.6-0.8	0	0.2-0.4	0.1-0.3

b. Percent increase in brake specific fuel consumption

Retard	5.2	4.3	3.6	1.2	3.4	1.0[c]	—	3.3[c]	2.2[c]
Air-to-Fuel	2.0	1.5	1.0	2.3	2.6	1.9	—	—	—
Derate	2.6	6.1	8.2[c]	1.1[c]	7.0[c]	—	3.4[c]	—	9.6
MAT	1.3	0.5	—	0	0.4	+0.5	—	1.6	0

[a] Baseline data in gm/kWh shaft output, all other data in percent NO_x reduction/unit control. Unit control is 1° retard, 1 percent air flow increase, 1 percent derating, or 1.8K (1.0F) air temperature decrease.

[b] BS - blower scavenged, TC - turbo-charged, NA - naturally aspirated.

[c] Average value

Numerous investigators have studied control techniques to reduce NO_x in diesel-fueled automotive truck applications. Many of these studies are summarized in Reference 4-57. Retard, turbocharging, aftercooling, derating and combinations of these controls are techniques that are currently utilized by manufacturers to meet California heavy-duty vehicle (>2700 kg, or 6000 lb) emission limits for diesel-fueled engines.

Table 4-21 lists five samples of NO_x control techniques currently implemented by truck manufacturers to meet the 1975 California 13.4 g/kWh* (10 g/hp-hr) combined NO_x and HC emission level. Manufacturers indicate that greater reductions will require (1) increasing degrees of application of these controls (and incurring additional fuel penalties) or, (2) application of techniques that need further development to overcome maintenance, control, and durability problems. Controls in this second category include EGR, water injection, and NO_x reduction catalysts.

Gasoline engine manufacturers, in response to Federal and State regulations, have also conducted considerable research of emission control techniques to reduce NO_x, as well as HC and CO, levels. Efforts in this area have been directed at reducing emissions to meet (1) Federal and California heavy-duty vehicle limits, and (2) Federal and California passenger car emissions limits. Table 4-22 lists Federal and State emission limits, and Table 4-23 lists the various controls that are used in several combinations by manufactures to meet these limits. Table 4-24 gives specific examples of control techniques recently applied to meet Federal light duty vehicle emission limits.

Based on the preceding discussion, potential NO_x emissions reductions for stationary reciprocating engines can be summarized as follows:

- Controls such as retard, air-to-fuel ratio change, turbocharging, inlet air cooling (or increased after cooling), derating and combinations of these controls have been demonstrated to be effective and could be applied with no required lead time for development. Fuel penalities, however, accompany these techniques and may exceed 5 percent of the uncontrolled consumption.
- Exhaust gas recirculation, water injection, catalytic conversion and precombustion or stratified charge techniques involve some lead time to develop as well as time to address maintenance and control problems.

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*rated shaft output

TABLE 4-21. CONTROL TECHNIQUES FOR TRUCK SIZE DIESEL ENGINES [<375 kW (500 HP)] TO MEET 1975 CALIFORNIA 13.4 G/KWHR (10 G/HP-HR) COMBINED NO_x AND HC LEVEL[a]

Control	Percent bsfc[b] Increase
Retard, modify fuel system and turbocharger	3 3
Retard, modify fuel system and turbocharger, add aftercooler	2
Add turbocharger and aftercooler[c]	3
Retard[c] (naturally aspirated version)	3
Precombustion chamber	5 - 8

[a] Based on Federal 13 mode composite cycle

[b] bsfc = brake specific fuel consumption

[c] Stationary versions of this engine would require a cylinder head with four exhaust valves rather than existing two valves.

TABLE 4-22. 1975 VEHICLE EMISSION LIMITS

	NO_x	HC	CO
Passenger Car, g/kWh (g/mi)[a]			
California	6 (2.0)	3 (0.9)	26 (9)
Federal	9 (3.1)	4 (1.5)	44 (15)
Light duty truck, g/kWh (g/mi)			
California	6 (2.0)	6 (2.0)	59 (20)
Federal	9 (3.1)	6 (2.0)	59 (20)
Heavy duty vehicles, g/kWh			
California	13		40
Federal	21		53

[a] Emissions limits are estimated in g/kWh from g/mi assuming an average of 38.4 km/hr requiring 8195 W (11 bhp) for the 7-mode composite cycle.

TABLE 4-23. EMISSION CONTROL TECHNIQUES FOR AUTOMOTIVE GASOLINE ENGINES

Control	Comment
NO_x:	
Rich or lean A/F ratio	Increased bsfc, HC, and CO
Ignition timing retard	Increased bsfc, HC, and CO, amount of control limited by potential exhaust valve damage
Exhaust gas recirculation (5 to 10 percent)	Increase bsfc and maintenance related to fouling, smoking limits degree of control
Catalytic convertors (reduction)	In developmental stage
Increased exhaust back pressure	Increase bsfc
Stratified combustion	Requires different cylinder head, increased bsfc
HC, CO:	
Thermal reactor	Very effective in reducing HC, CO
Catalytic convertor (oxidation)	Requires periodic catalyst element replacement
Exhaust manifold air injection	Increased bsfc to power air pump
Positive crankcase ventilation	Reduces HC evaporative losses

TABLE 4-24. EMISSION CONTROL SYSTEMS FOR CONVENTIONAL GASOLINE INTERNAL COMBUSTION ENGINES (ADAPTED FROM REFERENCE 4-57)

Number	Year	System	Fuel Penalty %[b]	Reduction Factors[b]			
				HC[c]	CO[c]	NO_x[c]	System Deterioration[d]
0	1972	EM°[a]	—	1 ± 0.375	1 ± 0.375	1 ± 20	L
1	1973 Federal	EM° + EI + FC + AI + EGR	7 ± 3	1.35 ± 0.30	1.0 ± 0.23	0.6 ± 0.10	L
2	1975 Federal	EM° + EI + IC + QHI + AI + EGR	5 ± 2	0.65 ± 0.15	0.55 ± 0.15	0.06 ± 0.10	L
3	1975 Calif.	EM° + EI + IC + QHI + EGR + AI + OC	8 ± 2	0.18 ± 0.05	0.15 ± 0.03	0.06 ± 0.10	M (HC, CO) L (NO_x)

[a] 1972 baseline engine: modifications included in the baseline engine configuration are retard, lean air-to-fuel, and reduced compression ratio.

Component Identification

EM - Engine modifications; retard, air-to-fuel, compression ratio
EI - Electronic ignition
FC - Fast choke
QHI - Quick heat intake
AI - Exhaust manifold air injection
EGR - Exhaust gas recirculation
IC - Improved carburetion
OC - Oxidizing catalyst

[b] Reduction factor defined as: $\frac{\text{control system emissions}}{\text{1972 baseline emissions}}$ based on LA-4 driving cycle

[c] All emissions data taken using or corrected to 1975 CVS-CH test procedure

[d] Deterioration of present systems; L = 10%, M = 10 - 30%, H = 30%

- NO_x control technology for automotive applications can be adapted to stationary engines; however, NO_x reductions and attendant fuel penalties for automotive applications are closely related to the load cycle, which in some cases may differ from stationary applications
- Viable control techniques may involve an operational adjustment, hardware addition, or a combination of both
- Additional research is necessary to
  - Establish controlled levels for gaseous-fueled engines (<75 kW/cylinder, or 100 hp/cylinder)
  - Establish controlled levels for medium-powered diesel and gasoline engines based on stationary application load cycles
  - Supplement the limited emissions data available for large bore engines

4.3.1.2 Costs

As discussed earlier, stationary engines are unregulated for gaseous pollutants. Consequently, few data are available for field-tested controlled engines, particularly for large (>375 kW or 500 hp) engines. Sufficient data exist, however, to give order or magnitude NO_x control costs for the following engine categories:

- Natural gas-, dual-, and diesel-fueled engines above 75 kW/cylinder (100 hp/cylinder)
- Small to medium (<75 kW/cylinder) diesel-fueled engines
- Gasoline-fueled engines (10 kW to 375 kW)

Costs for large stationary engines can be estimated based on Reference 4-58 and information supplied by Reference 4-56. These costs, however, relate to emission reduction achieved by engines tested in laboratories rather than to field installations. Reference 4-59 indicates, nevertheless, that these data are representative.

In contrast to the large stationary engines, more published cost data exists for smaller (<375 kW, 500 hp) gasoline and diesel engines which must meet State (California) and Federal emission limits for mobile applications. Stationary engines in this size range are versions of these mobile engines. Therefore, costs can be estimated based on a technology transfer from mobile applications to stationary service, keeping in mind that in some cases mobile-duty cycles (variable load) can differ from stationary-duty cycles (rated load). Hence, costs (e.g., fuel penalties) associated with a control technique used in a stationary application may vary from the mobile case.

Control costs for the three categories discussed above may include:

- Initial cost increases for control hardware and/or equipment associated with a particular control (e.g., larger radiator for manifold air cooling or more engines as a result of derating)
- Operating cost increases which consist of either increased fuel consumption and/or increased maintenance associated with NO_x control system
- Combinations of initial and operating cost increases

Control Costs for Large Bore Engines

Table 4-25 lists cost impacts for control techniques available to users of large stationary engines. These cost impacts may be related to actual installations using baseline data presented in Table 4-26. In practice, these figures vary depending on the application, but, in general, they are representative of the majority of applications. Basically, these controls involve an operating adjustment with the exception of derating and manifold air cooling, which would require hardware additions. Derating is not a viable technique for existing installations unless additional units can be added to satisfy total power requirements.

The impact of the above control costs may vary considerably given the following considerations:

- Standby (<200hr/yr) application control costs are primarily a result of initial cost increases due to the emission control, whereas continuous service (>6000 hr/yr) control costs are largely a function of fuel consumption penalties
- Controls which require additional hardware with no associated fuel penalty (e.g., manifold air-cooling) may be more cost effective in continuous service (>6000 hr/yr) than operating adjustments which impose a fuel penalty (e.g., retard, or air-to-fuel change)
- The price of fuel can affect the impact of a control which incurs a fuel penalty. For example, a control which imposes a fuel penalty of 5 percent for both gas and diesel engines has more impact on the diesel fueled engine because diesel oil costs about 40 percent more per Joule than natural gas. This impact will diminish if gas prices increase more rapidly than oil prices.

TABLE 4-25. COST IMPACTS OF NO_x CONTROLS FOR LARGE-BORE ENGINES

Control	Cost Impact
Retard	Increased fuel consumption, more frequent maintenance of valves
Air-to-fuel changes	Increased fuel consumption, more frequent maintenance of turbocharger
Derate	Fuel penalty, additional hardware, and increased maintenance associated with additional units
Manifold air cooling	Increased cost to enlarge cooling system, and increased maintenance for cooling tower water treatment
Combinations of above	Initial, fuel, and maintenance
Control techniques	Increases as appropriate

TABLE 4-26. TYPICAL BASELINE COSTS FOR LARGE (>75 kW CYLINDER) ENGINES[a]

Costs	Gas	Dual Fuel	Diesel
1. Initial,[b] \$/kW	174	174	174
2. Maintenance, \$/kWh	4×10^{-3}	4×10^{-3}	4×10^{-3}
3. Fuel and lube, \$/kWh	10×10^{-3}	10×10^{-3}	23×10^{-3}
Total Operating, 2 + 3	14×10^{-3}	14×10^{-3}	27×10^{-3}

[a] Based on Reference 4-58 and information supplied to Reference 4-56 by manufacturers.

[b] Includes basic engine and cooling system.

Control Costs for Small and Medium Gasoline- and Diesel-Fueled Engines

Control costs for these engines can be characterized by analogy to those incurred to meet State and Federal emission limits for automotive vehicles. Again, these costs consist of initial purchase price increases for control hardware and increased operating costs (fuel and maintenance cost increases).

Table 4-27 lists typical costs for techniques implemented for 1975 diesel-fueled truck engines. These costs are presented to indicate order of magnitude effects. More research is required to relate specific emission control reductions to initial and operating cost increases for stationary engine applications.

Table 4-28 gives control hardware costs to meet gasoline-fueled passenger vehicle emission limits through 1976. Note that cost increases correspond to increasingly more complex controls to meet more stringent emission limits.

TABLE 4-27. TYPICAL CONTROL COSTS FOR DIESEL-FUELED ENGINES USED IN HEAVY-DUTY VEHICLES (>2700 kg OR 3 tons)

Vehicles[a]	
Initial	
baseline: engine	\$40-\$67/kW (\$30-\$50/hp)
baseline: cooling system	8%-14% engine
turbocharger	\$4/kW (\$3/hp)
aftercooler	6%-10% engine
EGR	\$3-\$4/kW (\$2-\$3/hp)
Operating	
Fuel:	Fuel penalties range from 3 to 8 percent for various techniques. Typical present fuel cost: \$0.095/liter (\$0.36/gallon) #2 diesel or \$2.13-\$2.37/GJ (\$2.25-\$2.50/10^6 Btu).
Maintenance:	EGR system will require periodic cleaning. Note that turbocharged, aftercooled engines require additional maintenance for the turbocharger and aftercooler compared to a similarly rated naturally aspirated version.

[a] Based on information supplied to Reference 4-56 by manufacturers.

TABLE 4-28. ESTIMATES OF STICKER PRICES FOR EMISSIONS HARDWARE FROM 1966 UNCONTROLLED VEHICLES TO 1976 DUAL-CATALYST SYSTEMS (Reference 4-57)

Model Year	Configuration	Typical Hardware			
		Value Added	Price	Excise Tax	Sticker Price
1966	PCV-Crank Case	1.90	2.85	0.15	3.00
1968	Fuel Evaporation System	9.07	14.25	0.75	15.00
1970	Carburetor Air/Fuel Ratio	0.61	0.95	0.05	1.00
	Compression Ratio	1.24	1.90	0.10	2.00
	Ignition Timing	0.61	0.95	0.05	1.00
	Transmission Control System	2.49	3.80	0.20	4.00
	Total 1970				8.00
1971-1972	Anti-Dieseling Solenoid	3.07	4.75	0.25	5.00
	Thermo Air Valve	2.49	3.80	0.20	4.00
	Choke Heat Bypass	2.74	4.18	0.22	4.40
	Assembly Line Tests, Calif (1/10 vol)	0.18	0.57	0.03	0.60
	Total 1971-1972				14.00
1973	OSAC (Spark Advance Control)	0.48	0.95	0.05	1.00
	Transmission Changes (some models)	0.63	0.95	0.05	1.00
	Induction Hardened Valve Seats (4 and 6 cyl)	0.72	1.90	0.10	2.00
	EGR (11 – 14%) Exhaust Recirculation	5.48	9.50	0.50	10.00
	Air Pump – Air Injection System	27.16	43.32	2.28	45.60
	Quality Audit, Assembly Line (1/10 vol)	0.23	0.38	0.02	0.40
	Total 1973				60.00

TABLE 4-28. ESTIMATES OF STICKER PRICES FOR EMISSIONS HARDWARE FROM 1966 UNCONTROLLED VEHICLES TO 1976 DUAL-CATALYST SYSTEMS (Reference 4-57) (Concluded)

Model Year	Configuration	Typical Hardware			
		Added	List Price	Excise Tax	Sticker Price
1974	Induction Hardened Valve Seat V-8	0.72	1.90	0.10	2.00
	Some Proportional EGR (1/10 vol at $52)	3.21	4.94	0.26	5.20
	Precision Cams, Bores, and Pistons	2.44	3.80	0.20	4.00
	Pretest Engines — Emissions	1.80	2.85	0.15	3.00
	Calif. Catalytic Converter System (1/10 vol at $64)	4.02	6.08	0.32	6.40
	Total 1974				20.60
1975	Proportional EGR (acceleration-deceleration)	20.07	30.02	1.58	31.60
	New Design Carburetor with Altitude Compensation	7.52	14.25	0.75	15.00
	Hot Spot Intake Manifold	2.87	4.75	0.25	5.00
	Electric Choke (element)	2.67	4.75	0.25	5.00
	Electronic Distributor (pointless)	4.35	9.50	0.50	10.00
	New Timing Control	1.40	2.85	0.15	3.00
	Catalytic — Oxidizing-Converter	18.86	34.20	1.80	36.00
	Pellet Charge (6 lb at $2/lb)	12.00	20.52	1.08	21.60
	Cooling System Changes	1.17	1.90	0.10	2.00
	Underhood Temperature Materials	0.63	0.95	0.05	1.00
	Body Revisions Welding Presses	0.67	1.90	0.10	2.00
	Assembly Line Changes	0.13	0.95	0.05	1.00
	End of Line Test Go/No-Go	1.85	2.85	0.15	3.00
	Quality Emission Test	1.22	1.90	0.10	2.00
	Total 1975				138.20
1976	2 NO_x Catalytic Converters*	22.00	37.05	1.95	39.00
	Electronic Control[a]	28.00	47.50	2.50	50.00
	Sensors[a]	3.00	5.70	0.30	6.00
	Total 1976				134.00

[a] 1976 most common configuration

Figure 4-14 illustrates the effect of various control techniques on fuel economy. Fuel cost increases can be easily derived from typical gasoline costs, presently $0.55-0.75/gallon. In addition to this operating expense, control techniques utilizing catalysts and EGR require periodic maintenance.

Manufacturers, in addition, incur certification costs for gasoline and diesel-fueled engines which must meet State and Federal regulations. These costs are passed on to the user in the form of increased initial costs. Manufacturers of diesel-fueled engines report these costs range from $50,000 to $100,000 for a particular engine family. This can result in a $125 cost per engine based on a low sales volume family.

4.3.1.3 Energy and Environmental Impact

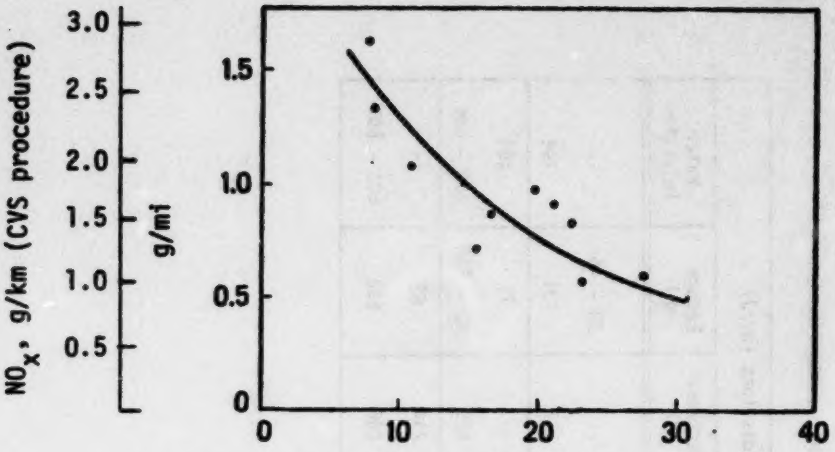
The energy impacts of applying NO_x controls to stationary reciprocating IC engines are manifested almost exclusively through corresponding increases in fuel consumption (bsfc). Typical percentage increases as a function of applied control were discussed in detail previously in Sections 4.3.1.1 and 4.3.1.2.

Potential adverse environmental impacts occur through increases in emissions of combustion-generated pollutants other than NO_x attendant to applying a NO_x control. Since IC engines emit only an exhaust gas effluent stream, impacts through liquid and solid effluents need not be considered. In addition, since IC engines fire "clean" fuels (natural gas and distillate oil) incremental effects on the emissions of such pollutants as SO_x and trace metals are relatively unimportant. Thus, the following discussion will focus on the measured effects of specific NO_x control techniques on incremental emission of CO, HC, and particulate (smoke). Again, all available data were obtained in tests on laboratory engines. Nevertheless, such data should be representative.

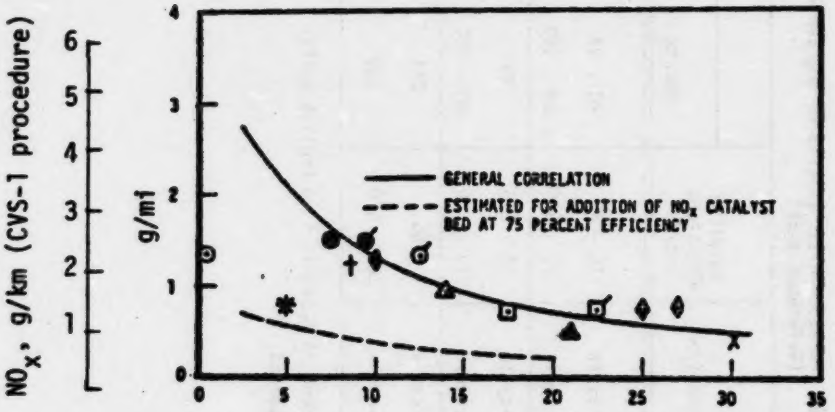
Carbon Monoxide

As discussed in Section 4.3.1.1, the most common NO_x reduction techniques applied to IC engines include derating, ignition retard, altering air/fuel (A/F) ratios, reducing manifold air temperatures (MAT), and water injection. The effects of each of these NO_x controls on engine CO emission levels are summarized in Table 4-29.

As indicated, baseline CO emissions from two-cycle engines are generally lower than those from four-cycle engines. However, derating two-cycle engines increases CO emissions 50 to 100 percent, while derating four-cycle engines actually gives a 60 to 100 percent decrease in CO levels.



a. Percent increase in BSFC (over uncontrolled vehicle) for constant volume sampling (CVS) tests with varying EGR and secondary air rates.



b. Percent increase in BSFC (over uncontrolled vehicle) for various driving cycles and control techniques.

Figure 4-14. Effect of NO_x emissions level on fuel penalty for light-duty trucks (Reference 4-59).

TABLE 4-29. REPRESENTATIVE EFFECTS OF NO_x CONTROLS ON CO EMISSIONS FROM INTERNAL COMBUSTION ENGINES[a] (Reference 4-56)

Fuel	Engine Type	Baseline Emissions (ng/J)	NO_x Control CO Emissions (ng/J)					
			Derate	Retard Ignition	Increase A/F	Decrease A/F	Reduce MAT	Water Injection
Natural Gas	2-cycle	15 - 40	40 - 94	35 - 45	29 - 31	--	29 - 45	--
	4-cycle	75 - 3350	54 - 150	80 - 1000	--[b]	117	131	194
Diesel	2-cycle	72 - 325	89	140 - 628	--	--	71	464
	4-cycle	114 - 546	100 - 180	260 - 654	439	675	142 - 550	460 - 606
Dual Fuel	2-cycle	165	244	244 - 267	--	244	67	--
	4-cycle	200 - 670	289	679 - 1070	288	296	632	503 - 507

[a] This table is included in Appendix A in English units.

[b] Denotes no data reported.

Retarding ignition generally causes increased CO output for all engines. This is somewhat expected, though, since retarding ignition decreases both peak combustion temperature and combustion gas residence time, which can lead to incomplete combustion. Both increasing A/F ratios and reducing manifold air temperature (MAT) has little effect on CO levels. However, decreasing A/F causes 50 to 100 percent increases in CO emissions. Water injection seems not to affect CO emissions from gas and dual fuel engines, but increases diesel engine CO emissions by 60 to 130 percent.

Hydrocarbons

The use of NO_x combustion controls on IC engines can also have significant effects on HC emissions, with different NO_x reduction techniques eliciting different effects.

As shown in Figure 4-15, derating causes HC emissions to increase, with the increase becoming more pronounced as load is further reduced. As the figure illustrates, derating can cause a 20 to 130 percent increase in HC emissions. Figure 4-16 shows the effect of ignition retard on incremental HC emissions. In contrast to the effects of engine derating, ignition retard tends to decrease slightly or not affect emissions of HC. However, in cases where retarding ignition initially reduces HC emissions, increasing the degree of ignition retard seems to have little further effect. The data in the figure indicate that HC emissions decrease on the average of 30 percent when ignition is retarded 3 to 8 degrees.

Changing the air-to-fuel (A/F) ratio, decreasing manifold air temperature (MAT) and water injection can all result in increased HC emissions. As shown in Figure 4-17, both increasing and decreasing the A/F ratio by 10 percent increases HC levels 20 to 65 percent. Larger percentage increases occur in engines with high baseline emissions. Figure 4-18 shows analogous effects when MAT is decreased. Decreasing 10 to 20 K (20 to 40 F) increases HC emissions 5 to 50 percent. HC levels increase as MAT is further reduced. Turbocharged engines exhibit the largest percentage emissions increases. Water injection also increases HC emissions from IC engines regardless of the baseline HC level, as shown in Figure 4-19. Average increases of 16 to 25 percent have been experienced for water/fuel (W/F) ratios of 0.1 to 0.25.

Particulates

Virtually no data are available specifically on particulate emission rates from stationary IC engines because it is difficult, time consuming, and expensive to measure particulate emissions from these engines directly. Instead, exhaust gas opacity readings have been used as a substitute measure of particulate emissions. These readings effectively measure particulate since a relationship between visible smoke and particulate mass emissions has been established for medium power

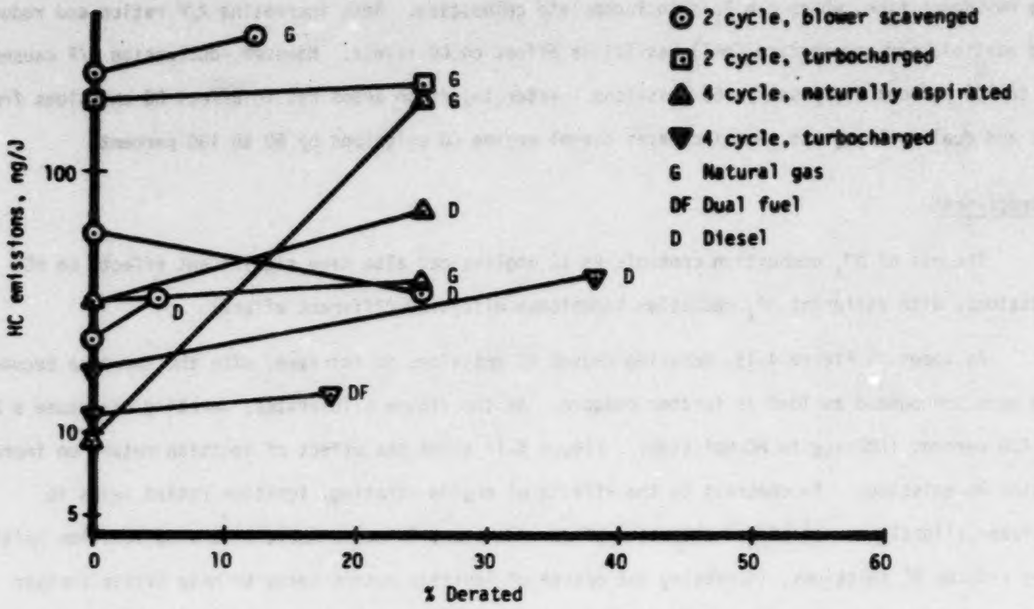


Figure 4-15. Effect of derating on IC engine HC emissions (Reference 4-56).

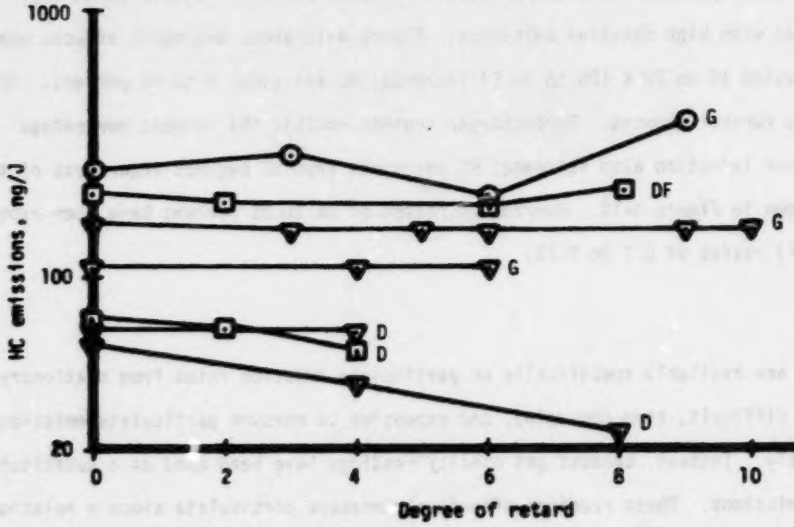


Figure 4-16. Effect of retarding ignition on IC engine HC emissions (Reference 4-56).

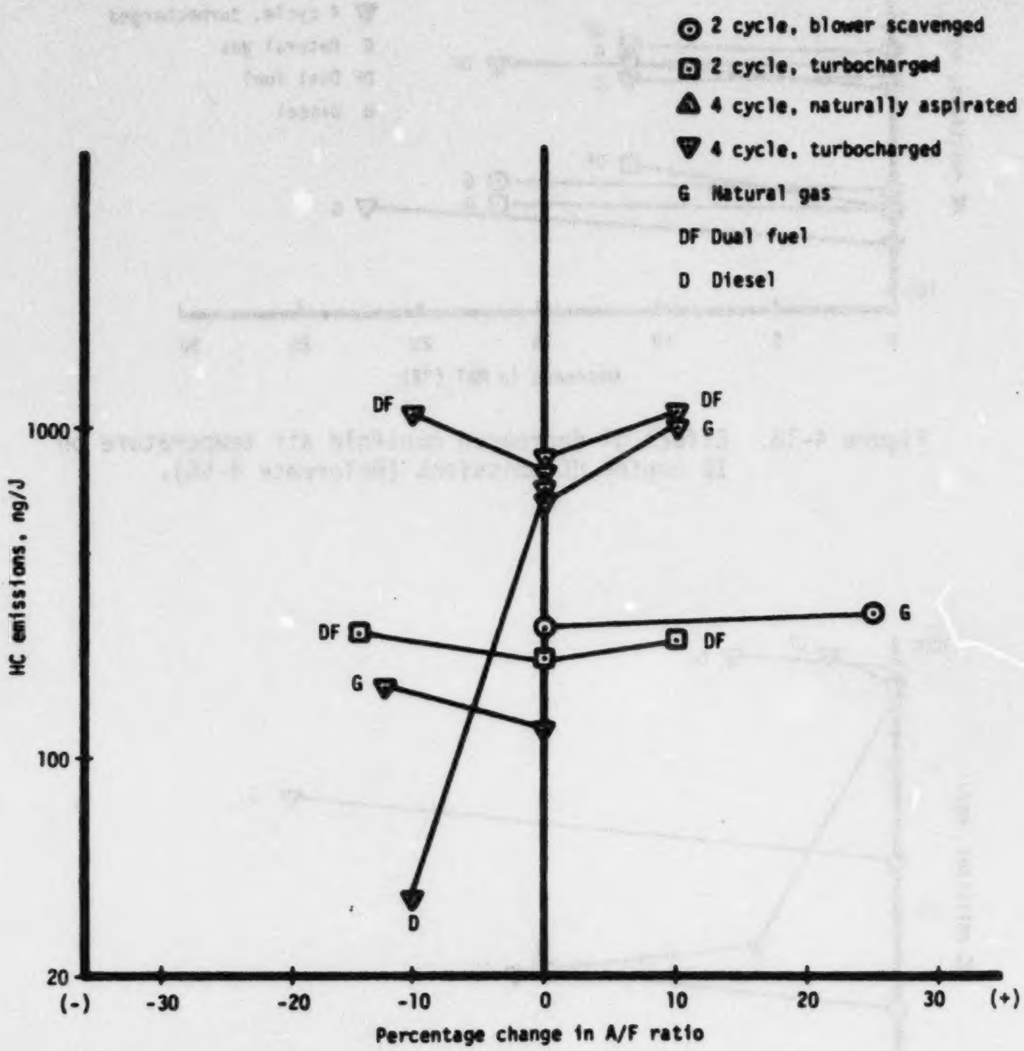


Figure 4-17. Effect of air-to-fuel ratio on IC engine HC emissions (Reference 4-56).

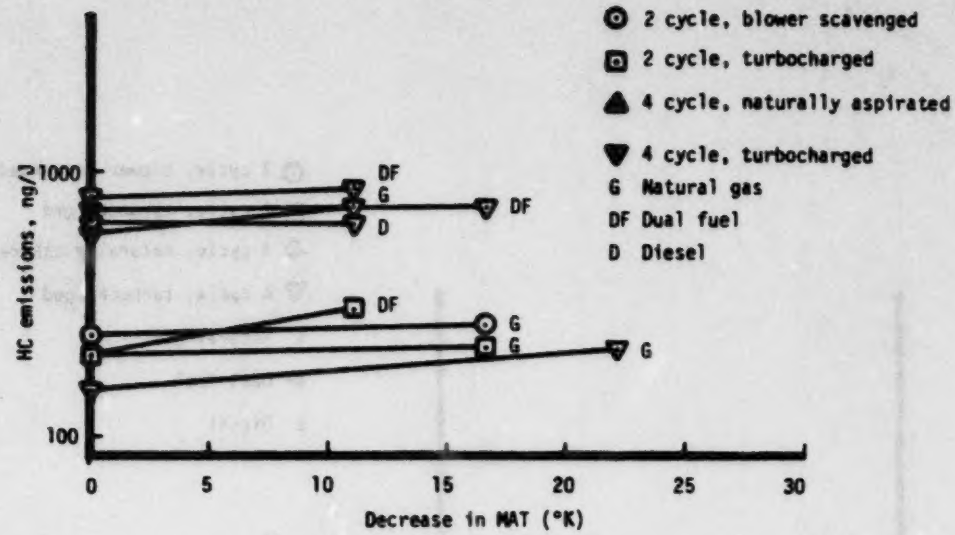


Figure 4-18. Effect of decreased manifold air temperature on IC engine HC emissions (Reference 4-56).

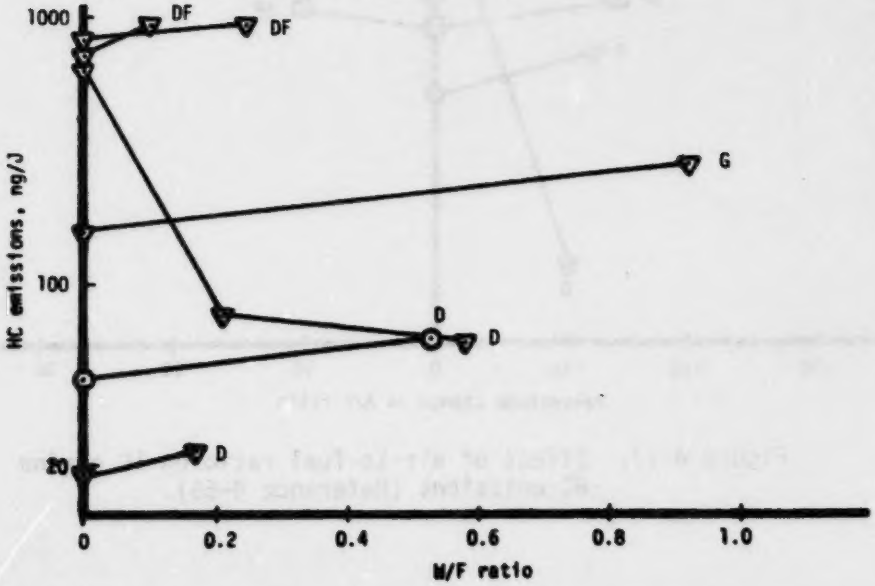


Figure 4-19. Effect of water injection on IC engine HC emissions (Reference 4-56).

diesel engines (Reference 4-60 and 4-61). Therefore, IC engine smoke emissions are generally reported as percent plume opacity, or as Bosch or Bacharach smoke spot numbers.

The plumes from most large-bore engines are nearly invisible when the engine is operating at steady-state. However, applying NO_x combustion controls can significantly affect smoke emissions. Figure 4-20 shows the relationship between smoke emissions and NO_x reduction as a function of NO_x control for those engines where data were reported on both pollutants. As the figure shows, NO_x controls, other than derating, generally increase smoke emissions, while derating decreases smoke levels. Ignition retard and exhaust gas recirculation (EGR) cause the most significant increases in smoke level.

Since NO_x controls which caused smoke levels to exceed 10 percent opacity were considered unacceptable in the tests summarized in Figure 4-20, none of the data points for controlled engines are above this value. However, the effect of progressively applying ignition retard and EGR on smoke emissions is best demonstrated by data which include higher smoke levels. Such data are presented in Table 4-30 for two-cycle diesel engines, and clearly show that smoke emissions increase progressively as percentage EGR or degree of retard is increased.

In summary, experimental data have shown that applying conventional combustion modification NO_x controls to IC engines can cause increases in CO, HC, and particulate (smoke) emissions. This is so because the combustion conditions required to prevent NO_x formation generally lead to less complete combustion.

4.3.2 Gas Turbines

Gas turbines contributed only 2 percent of the annual stationary source NO_x emissions in 1974, or 236 Gg (2.6×10^5 tons). They do, however, comprise a very rapidly growing source with increasing application in intermediate and base load power generation, pipeline pumping, natural gas compression, and onsite electrical generation. The increasing application of gas turbines carries with it the potential for increasing the NO_x emission contribution from these sources. In response to this, the frequency of control technique demonstration and implementation has increased in the past several years.

Uncontrolled NO_x emissions are a function of turbine size (or efficiency) and fuel type. Increasing the turbine size (or efficiency) increases the NO_x concentrations primarily due to higher combustion temperatures and to increased residence time at high temperatures. Oil-fired turbines generally have higher NO_x concentrations than gas-fired units. Typical uncontrolled NO_x emissions from gas turbines are illustrated in Figures 4-21 and 4-22 for large and small units, respectively.

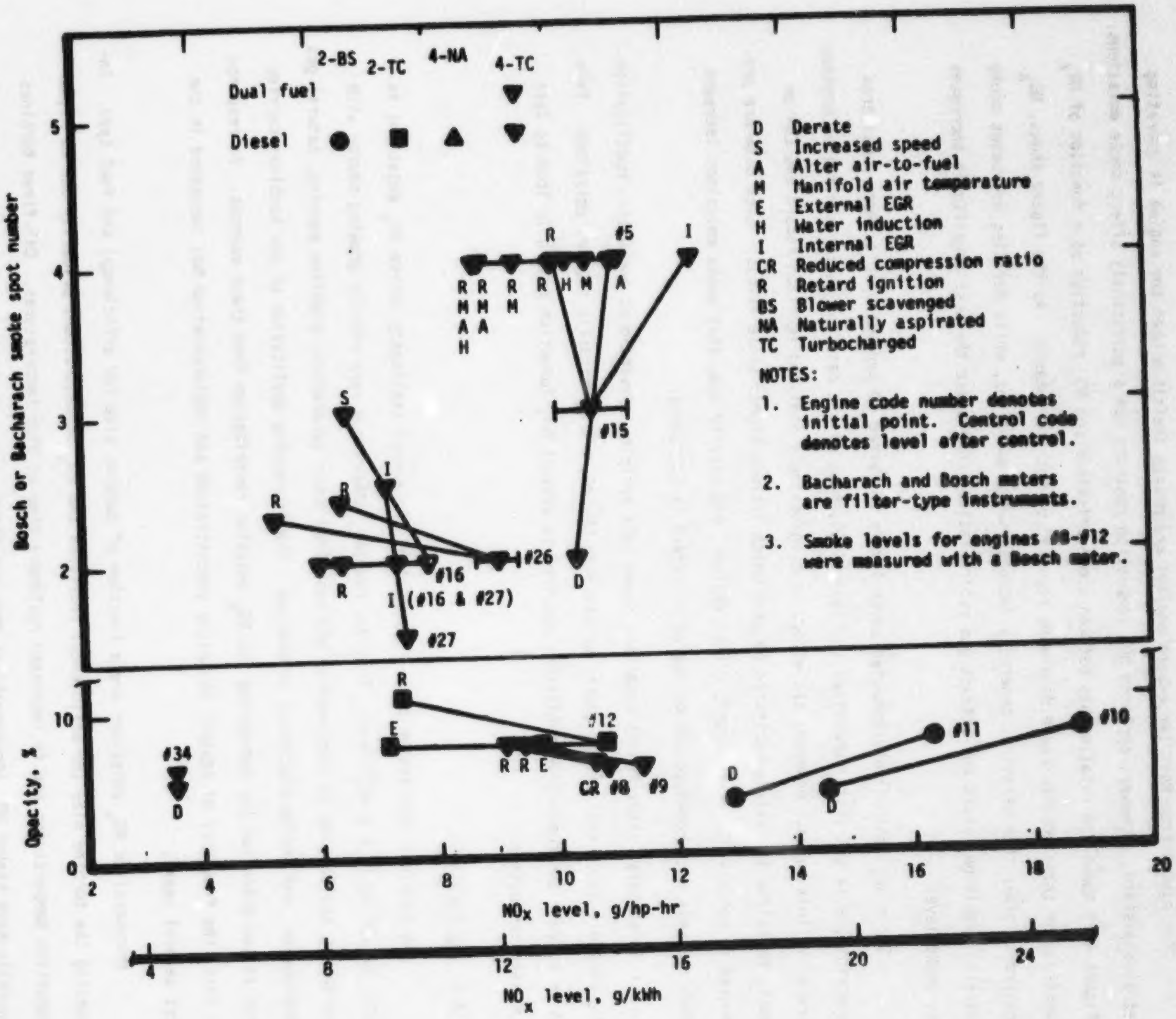


Figure 4-20. Smoke levels versus NO_x level for large-bore diesel engines (Reference 4-56).

TABLE 4-30. RELATIONSHIP BETWEEN SMOKE, EGR, AND RETARD (Reference 4-56).

Engine Type	Control [a]	Opacity, %
2-cycle, Blower Scavenged Diesel	None	4.7
	10% EGR	12
	20% EGR	27.5
	39% EGR	59
	4° advance[b]	2.7
	None	4.6
	4° retard	10
2-cycle, Turbocharged Diesel	None	7.5
	4.9% EGR	10.0
	8.4% EGR	11.5
	12.1% EGR	14.8

[a] All EGR data based on hot EGR.

[b] Injection advance is not a control; data included to show trend.

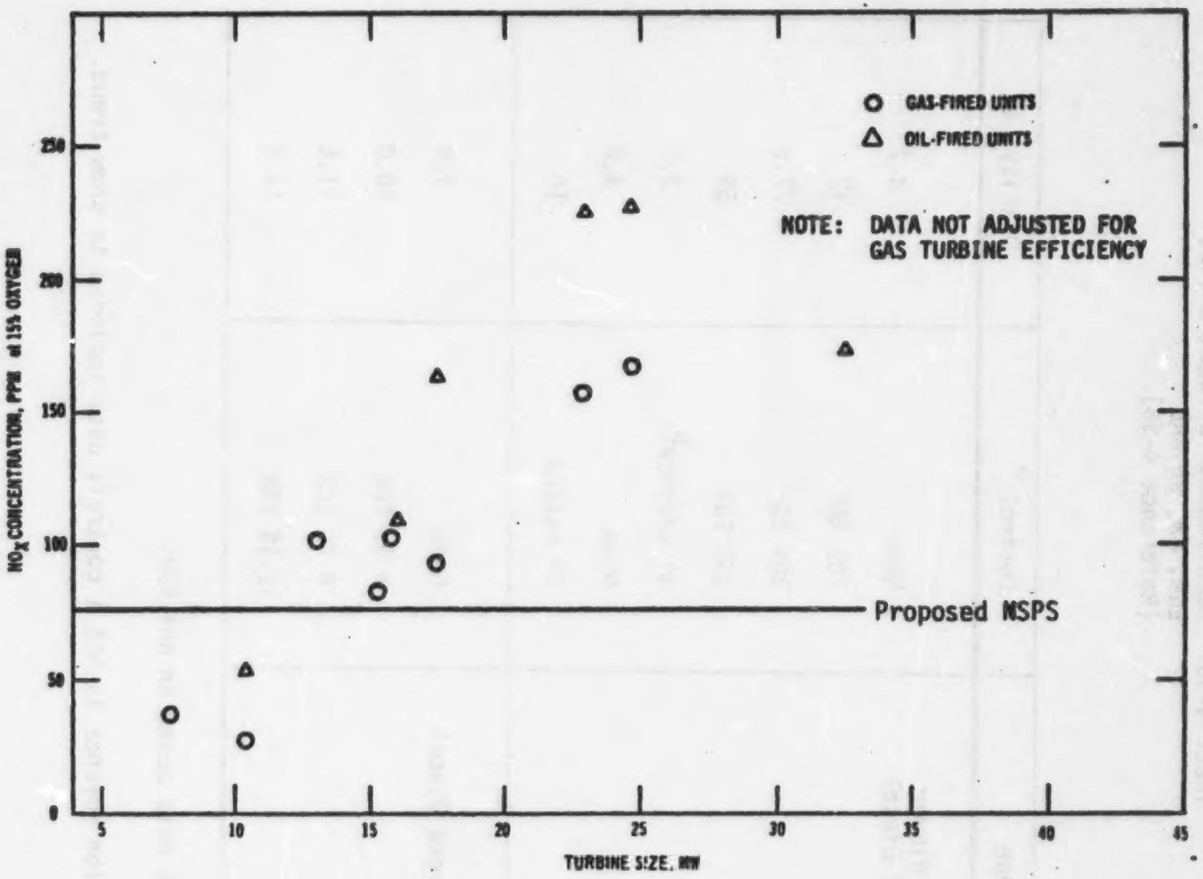


Figure 4-21. NO_x emissions from large gas turbines without NO_x controls (Reference 4-62).

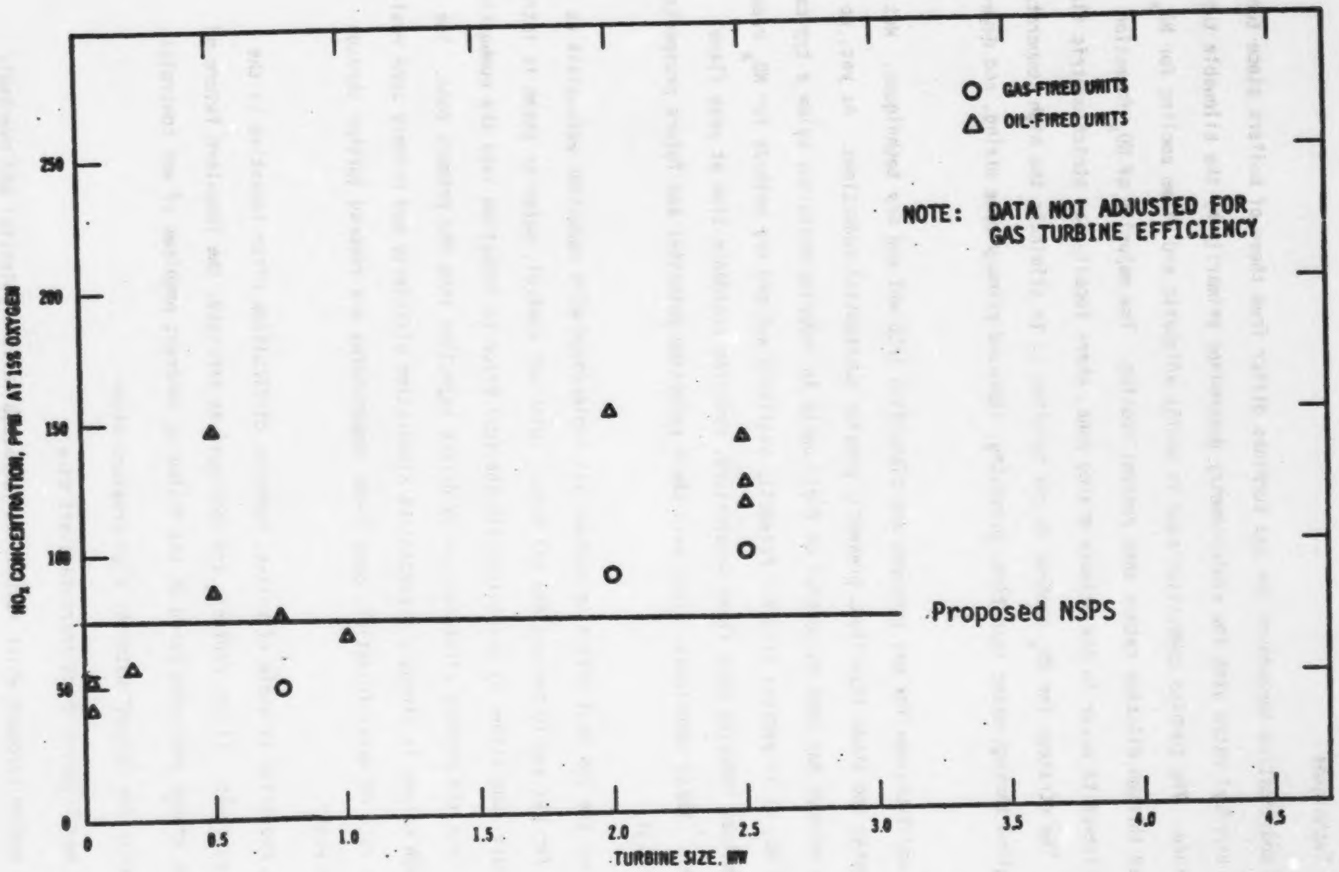


Figure 4-22. NO_x emissions from small gas turbines without NO_x controls (Reference 4-62).

Imposed on these figures is the proposed NSPS of 75 ppm for these sources. Very few units meet these standards in the uncontrolled state.

4.3.2.1 Control Techniques

Combustion modification techniques for gas turbines differ from those of boilers since turbines operate at a lean air/fuel ratio with the stoichiometry determined primarily by the allowable turbine inlet air temperature. The turbine combustion zone is nearly adiabatic and flame cooling for NO_x control is achieved through dilution rather than radiant cooling. The majority of NO_x formation in gas turbines is believed to occur in the primary mixing zone, where locally hot stoichiometric flame conditions exist. The strategy for NO_x control in gas turbines is to eliminate the high temperature stoichiometric regions through water injection, premixing, improved primary zone mixing, and downstreamed dilution.

Combustion modifications for gas turbines are classified into wet and dry techniques. Wet methods, such as water and steam injection, presently provide substantial reductions. As yet, no combination of dry methods has been successful on field units in reducing emissions below a typical standard of 75 ppm NO_x at 15 percent oxygen. Presently available wet and dry methods for NO_x reduction are aimed at either reducing peak flame temperature, reducing residence time at peak flame temperature, or both. These techniques, along with their reduction potential and future prospects, are shown in Table 4-31.

Wet techniques are the most effective methods yet implemented with reduction potentials as high as 90 percent for gas and 70 percent for oil fuels. With wet control, water or steam is introduced into the primary zone either by premixing with the fuel prior to injection into the combustion zone, by injection into the primary airstream, or by direct injection into the primary zone. The effectiveness of each method is strongly dependent on atomization efficiency and primary zone residence time. In the case of water injection, peak flame temperatures are reduced further through vaporization of the water.

Although NO_x reduction is quite effective, numerous difficulties offer incentive to the development of dry controls. If dry controls are developed as expected, the long-term future of wet control does not appear promising based on the following inherent problems of wet controls:

- Requirements for "clean" water or high-pressure steam
- Hardware requirements which increase plant size
- Delivery system hardware which results in increased failure potential and overhaul/maintenance time

TABLE 4-31. GAS TURBINE - SUMMARY OF EXISTING TECHNOLOGY - COMBUSTION MODIFICATIONS

Modification	Approach to NO_x Control	Reduction Potential	Near Term	Far Term	Additional Comments	Refs.
Wet Controls						
Water Injection	Lower peak flame temp by utilization of heat capacity and heat of vaporization; most effective when injected into primary flame zone	50-90+ %	To date, most effective measure, reasonable cost	Not as attractive as dry controls, but is adequate if dry not developed	Reduces efficiency, increases capital costs up to 10%. Operating costs as low as 1% depending on usage. Hindered by requirement for "clean" water supply. Ineffective in reducing fuel NO_x.	4-57 4-62 4-63 4-64
Steam Injection	Same as above	50-90+ %	To date, most effective measure after water injection	Same as above	Increases overall efficiency by increasing flowrate. Installation and operating costs same as water injection. Requires high pressure steam. Ineffective in reducing fuel NO_x.	
Dry Controls						
Lean Out Primary Zone	Lower peak flame temp	10-20%	Attractive option, requires additional controls to meet standards	Generally seen as an option to be incorporated into new low NO_x designs	Possible decrease in power output, less control over flame stabilization	4-57 4-62 4-64
Increase Mass Flowrate	Reduce residence time at peak temperatures	To 15%	Attractive option if feasible	Not an attractive long term option due to inflexibility	Possible increase in shaft speed constant torque	4-62
Earlier Quench with Secondary Air	Reduce residence time	To 15%	Minor combustor modification used presently with wet controls	An attractive concept to be employed in advanced combustors	An attractive option both for near term minor combustor modifications and for incorporation into new designs. Limited by flowrates and incomplete combustion.	4-57 4-62 4-65
Air Blast or Air Assist Atomization	Reduce peak flame temp by increasing mixing thereby reducing local A/F ratio	To ~90%	Limited application for retrofit	Promising method to be incorporated into new low NO_x design	Generally considered a new design concept	4-62
Reduce Inlet Preheat (Regenerative)	Reduce peak flame temp	Not Available	Not attractive due to thermal efficiency reduction	Not attractive for long term solution	Reduces efficiency.	4-62
Other Minor Combustor Modifications and Retrofit	Reduce peak flame temp through premixing, secondary air injection, primary zone flow recirculation	To 60% Combined	Attractive near term as an interim solution	Unknown at this time	With proper design, efficiency unimpaired	4-62
Exhaust Gas Recirculation	Reduce peak flame temperatures	To 38%	Option has seen use in minor combustor modifications	An attractive option for future design with internal combustors	Reduced efficiency requires additional controls.	4-62
Catalytic Combustion	Complete combustion at lower peak temperatures	To 98%	Technology not available	Attractive method for new combustor designs	Current research aimed at reducing reliability, maintainability, lifetime and start-up	4-62

- Uncertainty regarding long-term control effects on turbine components.

Although few combinations of presently available dry controls have the NO_x reduction potential of the wet methods, many dry techniques are used in conjunction with water or steam injection, particularly on larger units. On the smaller units, dry controls may be sufficient to meet standards. The dry controls now available are:

- Lean out primary zone — Reduces NO_x levels up to 20 percent by lowering peak flame temperatures. This option allows less control over flame stabilization and reduces power output but is an attractive control to be built into future low NO_x combustors.
- Increase mass flowrates — Possible NO_x reductions up to 15 percent by reducing residence time at peak flame temperature. This control essentially increases the turbine speed at constant torque and is not feasible in many applications.
- Earlier quench with secondary air — This is a minor combustor modification which entails upstream movement of the dilution holes to reduce residence time at peak temperatures. This is a promising control which is generally employed in advanced combustor research.
- Reduce inlet air preheat — A control applicable only to regenerative cycle units. It is not attractive due to reduction in efficiency.
- Air blast and air assists atomization — Use of high-pressure air to improve atomization and mixing requires replacement of injectors and addition of high-pressure air equipment. This control is considered an excellent candidate for incorporation into new low NO_x design combustors.
- Exhaust gas recirculation — Possible NO_x reduction of 30 percent. A candidate dry control for future design, though it has limited application in some online units. EGR requires extensive retrofit relative to other dry controls and also requires a distinct set of controls for the EGR system.

Other minor combustor modifications are generally aimed at providing favorable interval flow patterns in the primary zone and fuel/air premixing. The bulk of these modifications are combustor-specific and are being investigated by the manufacturer. In general, dry controls available for immediate implementation have not exceeded 40 percent NO_x reduction and as such may be insufficient controls for the larger units at present. Since dry techniques approach NO_x reduction differently than do wet controls, their effects are complementary and, consequently, can be used together. Figure 4-23 illustrates the effect of dry and wet controls used separately and in combination

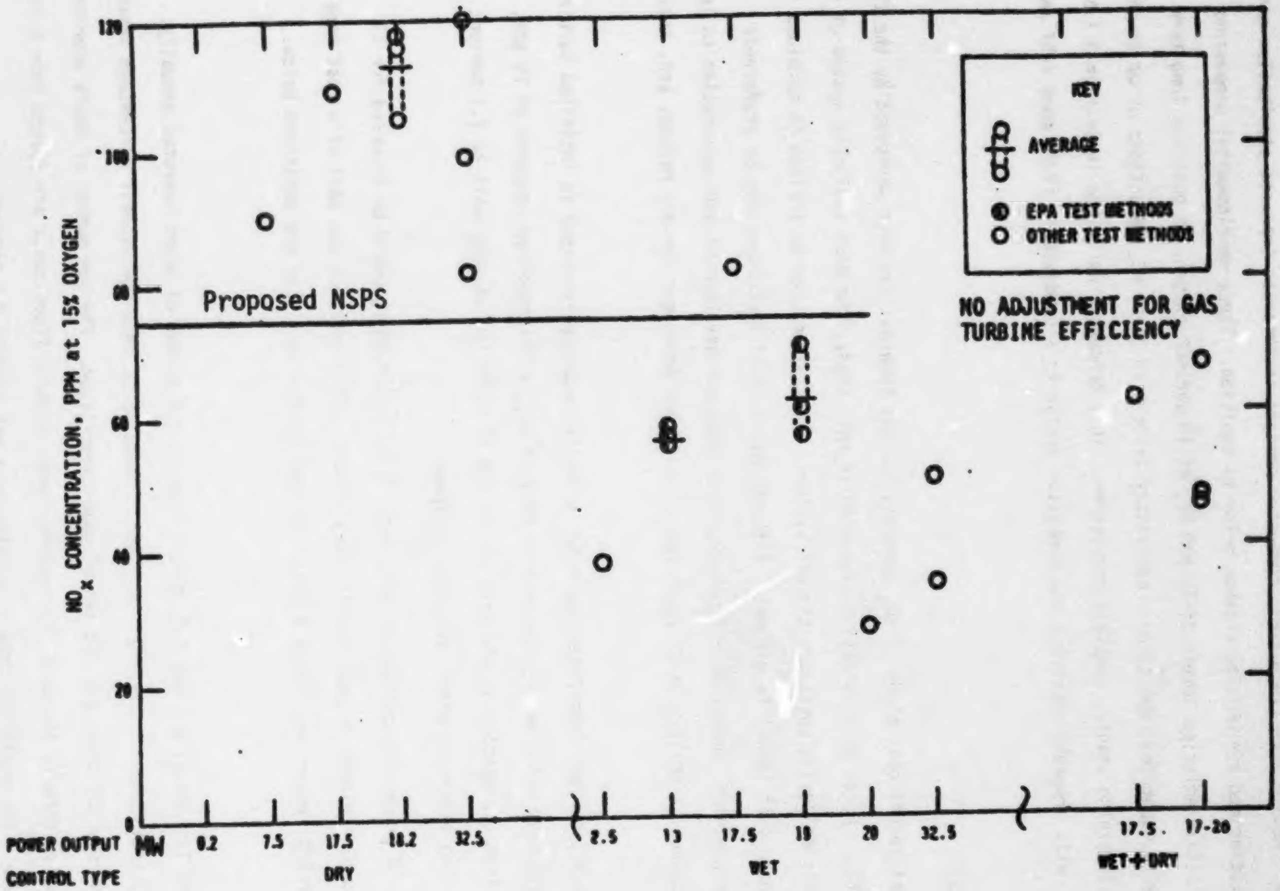


Figure 4-23. NO$_x$ emissions from gas turbines having NO$_x$ controls and operating on liquid fuels (Reference 4-62).

for liquid fuels (Reference 4-62). The figures show dry controls to be not sufficiently developed to meet the standards, whereas wet controls are sufficient.

Future NO_x control in gas turbines is directed toward dry techniques with emphasis on combustor design. Medium term (1979-1985) combustor designs incorporate improved atomization methods or prevaporization and a premixing chamber prior to ignition. These developmental combustors are projected to attain emission levels of 20 ppm NO_x at 15 percent oxygen. A possible long term option is catalytically supported combustion. Laboratory tests have given NO_x reductions of up to 98 percent while maintaining stable, complete combustion. This concept — described in Section 3.1.5.2 of this report — will probably require a new combustor design to accomodate it (Reference 4-57 and 4-62).

4.3.2.2 Costs

The most recent cost study of NO_x controls for gas turbines has been performed by the EPA (Reference 4-62). Based on information presented in this study, the best available system of emission reduction considering costs are the wet systems. Wet systems can be applied to turbines immediately and their cost impact is minimal. Although dry control techniques may be preferable because of their minimal impact on efficiency, their complete development and application to large production turbines is still several years away. Cost considerations for dry methods are, therefore, not discussed.

Table 4-32, derived from Reference 4-62, shows the expected increase in installed turbine cost that will result from using water injection to control NO_x to the proposed standard of 75 ppm. The impact varies from 0.8 percent in the case of the 820 kW (1100 hp) standby unit to 7.1 percent for the unit requiring extensive water treatment equipment.

Table 4-33 presents a summary of the costs in mills/kWh which would be incurred for 11 simple cycle turbine plants to meet the 75 ppm standard. This analysis was part of a cost model developed in an EPA report (Reference 4-62). The results for each case are explained below.

Standby Units

The first two cases, S-1 and S-2, differ only in the number of hours operated annually. Unit S-1 operates 80 hours and S-2 200 hours per year. These units show the highest percentage impact in terms of the incremental costs per net kWh of power generation. The low number of hours operated each year tends to increase the cost of producing power because fixed costs are spread over a relatively small base. The estimated impact in both cases was roughly 2.4 percent.

TABLE 4-32. IMPACT OF NO_X EMISSION CONTROL ON THE INSTALLED CAPITAL COST OF GAS TURBINES (Reference 4-62)

Application	Installed Cost (1000$)		% Increase
	Uncontrolled	Controlled	
A. Standby			
1. 260 kW[a] (350 hp)	55.6	58.0	2.4
2. 820 kW[a] (1100 hp)	177.9	179.3	0.8
B. Industrial			
1. 3 MW[a] (4000 hp) — typical	352.8	366.8	4.0
2. 3 MW[a] — offshore	352.8	379.8	7.1
C. Utility			
1. 66 MW[b]	9900.0	10070.0	1.7

[a] shaft output

[b] electrical output

TABLE 4-33 WATER INJECTION COSTS, MILLS/kWh (Reference 4-62)

Item	Standby				Industrial			Utility				Offshore Drilling Platform
	S-1	S-2	S-3	S-4	I-1	I-2	I-3	U-1	U-2	U-3	U-4	
Unit Size	260 kW	260 kW	820 kW	820 kW	3 MW	3 MW	3 MW	66 MW	66 MW	66 MW	6 MW	11 GJ/hr
Hours of Operation Per Year	80	200	80	200	2000	2000	3000	200	500	2000	8000	8000
Annualized Fixed Costs	13.65	5.46	4.32	1.73	0.48	0.12	0.12	2.58	1.03	0.26	0.06	0.23
Operating Cost of Water Treatment	0.46	0.46	0.37	0.37	0.10	0.10	0.10	0.11	0.11	0.11	0.11	0.35
Water for Injection	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	—
Energy Penalty	0.51	0.51	0.51	0.51	0.43	0.43	0.43	0.34	0.34	0.34	0.34	0.43
Water Transport Costs	—	—	—	—	—	—	0.64	—	—	—	—	—
Output Enhancement	—	—	—	—	—	0.09	0.09	—	—	—	0.11	0.09
Total	14.63	6.44	5.21	2.62	1.02	0.57	1.21	3.04	1.49	0.72	0.41	0.92
Baseline Costs	611.29	264.79	611.29	264.79	43.77	32.53	35.53	180.00	85.45	38.20	26.39	32.53
Percent Impact	2.39	2.43	0.85	0.99	2.32	1.75	3.71	1.69	1.75	1.88	1.56	2.83

[a] Utility turbine size as electrical output, others as shaft output

Cases S-3 and S-4 are 820 kW (1100 hp) units operating the same number of hours, respectively, as the smaller 260 kW units. These units can use exactly the same water purification system as the smaller units. Since the costs of producing power independent of the water injection system (the baseline cost) are identical between cases S-1 and S-3 and S-2 and S-4, the percentage impact of NO_x control is decreased to less than one percent.

Industrial Units

Case I-1 represents a normal, single shaft gas turbine application. The unit is operated 2000 hours per year and is slightly oversized. This negates any benefits that might be derived from improved unit output. For Case I-2, also a baseload turbine, a credit was taken for the improved capacity of the unit.

The highest cost impact was recorded in Case I-3, which represents a remote turbine application in an arid climate in which water must be transported fifty miles at a cost of 2¢ per gallon. The impact in such cases, including water storage facilities, is approximately a 3.7 percent increase in the average cost of generating power. Since water injection results in a slight increase in the power output capacity of the unit, a credit of 0.05 mills per kWh was taken for the output enhancement.

Utility Applications

The first unit operated 200 hours, the second 500 hours, the third 2000 hours, and the fourth 8000 hours annually. A credit for enhanced output was taken in the last case, since the unit is baseloaded. In all four cases, the impact is less than 2 percent.

Offshore Drilling Platform

Initially, it was thought that this case would evidence the highest cost impact. The unit was assumed to use sea water to fuel the water purification system, resulting in a substantial increase in the capital and operating cost of the system. The installed cost of the water treatment equipment was $27,000, compared to $14,000 for an onshore application. Despite these higher costs, the availability of water offset the costs associated with transporting water to the remote gas compressing station application (I-3). The total cost of water injection for the offshore platform was 0.92 mills/kWh compared to 1.21 mills/kWh for the remote site.

In the EPA cost model, no attempt was made to provide detailed estimates of the control costs for regenerative and combined cycle gas turbines. The cost impacts, in absolute terms, are not expected to be much greater than for simple cycles. Indeed, the percentage impacts will be less, given the higher cost per kW of generating capacity of these units.

In summary, the resulting estimates showed that, except for standby units, the total change in costs will probably fall in the range of 0.4 to 1.5 mills per kWh for turbines used in industrial and utility applications. This cost is equivalent to about a 2 percent increase in operating costs. Control costs for standby units were much higher, ranging from 2 to 14 mills per kWh. This is primarily due to their low use factor. This cost is equivalent to approximately a 2.5 percent increase in operating costs.

4.3.2.3 Energy and Environmental Impact

As was the case for reciprocating IC engines, the energy impacts of applying NO_x controls to gas turbines occur almost solely through effects on unit fuel consumption, which were noted in the foregoing discussion. Dry controls, except for reduced air preheat applied to regenerative cycle turbines, have insignificant effects on unit efficiency. On the contrary, wet controls can impose energy penalties. Water injection at the rate of 1 kg H_2O/Kg fuel reduces turbine efficiency by about 1 percent. If waste steam is available, steam injection can increase turbine efficiency by increasing turbine power output at constant fuel input. But, if a fuel debit is taken for heat needed to raise injection steam, overall plant efficiency losses comparable to those experienced with water injection will occur.

Again, as with IC engines, gas turbines emit only an exhaust gas effluent stream and fire "clean" fuels. Thus the potential environmental impacts of NO_x controls applied to gas turbines will occur through incremental effects on emissions levels of exhaust gas CO, HC, and particulate (smoke). Effects through liquid and solid effluents need not be considered, and incremental impacts on SO_x, trace metal, and, to some extent, higher molecular weight organic emissions are insignificant.

The effects of some commonly applied NO_x control techniques on CO emissions from gas turbines are summarized in Table 4-34. From the table, it is apparent that dry controls, notably leaning the primary zone and air blast (or air-assist atomization) reduce CO levels. This is expected since the additional air introduced into the combustor when applying these techniques allows more complete fuel combustion. On the other hand, wet control techniques, such as water injection, tend to quench combustion and give lower combustor temperatures. This leads to incomplete combustion and increased CO levels as shown in Table 4-34.

The very limited data on incremental hydrocarbon emissions due to NO_x combustion controls applied to stationary gas turbines are summarized in Table 4-35. As the table shows, the effects of dry NO_x controls are mixed. Air blast tends to increase HC emissions while leaning the primary zone tends to decrease HC levels. Increased combustion efficiency due to higher combustion

TABLE 4-34. REPRESENTATIVE EFFECTS OF NO_x CONTROLS ON CO EMISSIONS FROM GAS TURBINES (Reference 4-62)

NO_x Control	Fuel	CO Emissions (ppm)[a]	
		Baseline	NO_x Control
Lean Primary Zone	Natural Gas	102	51
	Kerosene	102	96
	Diesel	53	99
		195	59
Air Blast/ Piloted Air Blast	Kerosene	969	110
	Diesel	53	36
Water Injection	Natural Gas	147	1134
		252	1512
	Diesel	99	144
		135	162
		93	30

[a] 3% O_2, dry basis. Emissions levels at full load.

TABLE 4-35. SUMMARY OF THE EFFECTS OF NO_x CONTROLS ON VAPOR PHASE HYDROCARBON EMISSIONS FROM GAS TURBINES (Reference 4-62)

NO_x Control	Fuel	HC Emissions (ppm)[a]		Comment
		Baseline	NO_x Control	
Air Blast	Jet-A	18	41	Idle
		9	11	Full load
Lean Primary Zone	Natural Gas	33	9 - 12	
	Diesel Fuel	30	12	Full load
		3	7	
	Kerosene	27	12	
Water Injection	Natural Gas	234	372	
		141	246	W/F = 0.5
		36	27	
	Diesel Fuel	24	12	

[a] 3% O_2, dry basis.

temperatures tends to support this latter observation. The effects of applying wet controls are also mixed. As indicated in the table, with water injection at a water-to-fuel (W/F) weight ratio of 0.5, HC emissions increased for turbines having high baseline HC emissions, but decreased for turbines which emitted low baseline HC levels.

The data on particulate emissions from gas turbines resulting from applied NO_x controls are also very limited and are as inconclusive regarding the increment in particulate emissions from NO_x controls as those for incremental CO and hydrocarbon emissions. For example, the effect of water injection on particle emissions seems to be related to the specific injection method used (Reference 4-62). Some tests show smoke level reduction of 1.5 to 1.75 smoke spot numbers when water injection is used. Other tests, however, indicate increased particulate emissions with water injection at peak load.

In summary, the limited data available on the incremental effects of NO_x controls on CO, HC, and particulate emissions suggest that the control techniques do not significantly affect these emissions. While dry techniques appear to decrease CO emissions and wet controls seem to increase CO levels, even these data, as well as those on effects on HC and particulate levels, are inconclusive.

4.4 SUMMARY

Table 4-36 summarizes current and emerging NO_x control technology for the major source categories. These results show that current technology is dominated by combustion process modification. Emerging technology is also centered around combustion modifications. Other approaches, such as flue gas treatment, may be used in the 1980's to augment combustion modification if required by stringent emission standards.

The level of combustion modification control available for a given source depends on the importance of that source in regulatory programs. Utility boilers have been the most extensively regulated and accordingly, the technology is the most advanced. Available technology ranges from operational adjustments such as low excess air and biased burner firing to inclusion of overfire air ports or low NO_x burners in new units. Some adverse operational impacts have been experienced with the use of combustion modification on existing equipment. In general these have been solved through combustion engineering or by limiting the degree of control application. With factory-installed controls on new equipment, operational problems have been minimal.

The technology for other sources is less well developed. Control techniques shown effective for utility boilers are being demonstrated on existing industrial boilers. Here, as for utility

TABLE 4-36. SUMMARY OF NO_x CONTROL TECHNOLOGY (Reference 4-34)

Equipment/ Fuel Category	Current Technology				Emerging Technology		Comments
	Available Control Technique	Achievable NO_x Emission Level ng/J (lb/10^6 Btu)	Estimated Differential Annual Cost	Operational Impact	Near-Term 1977-1982	Far-Term 1983-2000	
Existing coal-fired utility boilers	LEA + OSC (OFA, BOOS, BBF); new burners	260-300 (0.6 - 0.7)	20-30¢/kW	Possible increase in corrosion & slagging & carbon in flyash	Advanced low-NO_x burners	Ammonia injection; flue gas treatment	Ammonia injection, FGT potential supplement to CM if needed
New coal-fired utility boilers	LEA + OFA; new burners	215-260 (0.5 - 0.6)	10-20¢/kW	No major problem with tangential design; other designs now coming online	Low-NO_x burners advanced staging concepts	Optimized burner firebox design; fluidized bed combustion; ammonia injection	Same as above
Existing oil-fired utility boilers	LEA + OSC + FGR; load reduction	110-150 (0.25 - 0.35)	\$1-2/kW	Possible flame instability; boiler vibration	Low-NO_x burners; oil denitrification	Ammonia injection; flue gas treatment	No new units; emission levels are limit of current technology
Existing gas-fired utility boilers	LEA + OSC + FGR; load reduction	65-85 (0.15 - 0.2)	\$1-2/kW	Possible flame instability; boiler vibration	Low-NO_x burner	Ammonia injection; flue gas treatment	No new units; emission levels are limit of current technology
Oil-fired industrial watertube boilers	LEA + OSC (OFA, BOOS, BBF)	85-130 (0.2 - 0.3)	7-9¢/(kg/hr)[a]	~1% increase in fuel consumption; flame instability; boiler vibration (retrofit)	Low-NO_x burners; OFA in new unit designs; oil denitrification	Optimized burner/firebox design; ammonia injection	Current technology still being developed

[a] kg/hr steam produced

TABLE 4-36. SUMMARY OF NO_x CONTROL TECHNOLOGY (Concluded)

Equipment/ Fuel Category	Current Technology				Emerging Technology		Comments
	Available Control Technique	Achievable NO_x Emission Level ng/J ($lb/10^6$ Btu)	Estimated Differential Annual Cost	Operational Impact	Near-Term 1977-1982	Far-Term 1983-2000	
Stoker-fired industrial watertube boilers	LEA + OFA	150-190 (0.35 - 0.45)	9-11¢ (kg/hr)[a]	Possible ~1% increase in fuel consumption; corrosion; slagging of grate (retrofit)	Inclusion of OFA in new unit design	Fluidized bed combustion; ammonia injection	Current technology still being developed
Gas-fired industrial watertube boilers	LEA + OSC (OFA, BOOS, BBF)	86-130 (0.2 - 0.3)	7-9¢/ (kg/hr)[a]	~1% increase in fuel consumption; flame instability; boiler vibration (retrofit)	Low-NO_x burners; OFA in new unit design	Optimized burner/firebox design; ammonia injection	Current technology still undergoing development
Industrial firetube boilers	LEA + FGR; LEA + OSC	65-110 (0.15 - 0.25)	30-65¢/ (kg/hr)[a]	~1% increase in fuel consumption; flame instability (retrofit)	Low-NO_x burners; OFA or FGR in new unit design	Optimized burner/firebox design	Development continuing on current technology
Gas turbines	Water, steam injection	110-150 (0.25 - 0.35)	$1-2/kW	~1% increase in fuel consumption; affects only thermal	Advanced combustor designs for dry NO_x controls	Catalytic combustion; advanced can designs	Current technology widely used
IC engines	Fine tuning; changing A/F	1,070-1,290 (2.5 - 3.0)	$0.70-2.00/kW ($0.50-1.50/BHP)	5-10% increase in fuel consumption; misfiring; poor load response	Include moderate control in new unit design	Advanced head designs	Technology still being tested

[a] kg/hr steam produced

boilers, the emphasis in emerging technology is on development of controls applicable to new unit design. Advanced low NO_x burners and/or advanced off-stoichiometric combustion techniques are the most promising concepts. This holds true for the other source categories as well. The R&D emphasis for gas turbines and reciprocating IC engines is on developing optimized combustion chamber designs matched to the burner or fuel/air delivery system.

REFERENCES TO SECTION 4

4-1 Lachapelle, D. G., J. S. Bowen, and R. D. Stern, "Overview of the Environmental Protection Agency's NO_x Control Technology for Stationary Combustion Sources," presented at the 67th AIChE Annual Meeting, December 1974.

4-2 Teixeria, D. P., R. E. Thompson, "Utility Boiler Operating Modes for Reduced Nitric Oxide Emissions with Oil Fuel Firing," presented at the 66th Annual Meeting of the Air Pollution Control Association, Chicago, June 1973.

4-3 Bartok, W., et al., "Systematic Field Study of NO_x Emission Control Methods for Utility Boilers," Esso R & E, Report GRU.4GNOS.71, December 31, 1971.

4-4 Barr, W. H., "Nitric Oxide Control — A Program of Significant Accomplishments," ASME Paper 72-WA/PWR-13, 1972.

4-5 Blakeslee, C. E., "Reduction of NO_x Emissions by Combustion Modifications to a Gas-Fired 250-MW Tangential Fired Utility Boiler," presented at Conference on Natural Gas Research and Technology, Atlanta, Georgia, June 5-7, 1972.

4-6 Blakeslee, C. E. and H. E. Burbach, "Controlling NO_x Emissions from Steam Generation," JAPCA, Volume 23, No. 1, January 1973.

4-7 Halstead, C. J., et al., "Nitrogen Oxides Control in Gas-Fired Systems Using Flue Gas Recirculation and Water Injection," IGT/AGA Conference on Natural Gas Research and Technology, Atlanta, Ga., June 1972.

4-8 Bagwell, F. A., et al., "Utility Boiler Operating Modes for Reduced Nitric Oxide Emissions," JAPCA, Volume 21, No. 11, November 1971.

4-9 Habelt, W. W., and A. P. Selker, "Operating Procedures and Prediction for NO_x Control in Steam Power Plants," presented at Central States Section of the Combustion Institute, Spring Meeting, March 1974.

4-10 Norton, D. M., K. A. Krumwiede, C. E. Blakeslee, and B. P. Breen, "Status of Oil-Fired NO_x Control Technology," In: The Proceedings of the NO_x Control Technology Seminar, EPRI Special Report, SR-39, February 1976.

4-11 Barr, W. H., F. W. Strehlitz, and S. M. Dalton, "Retrofit of Large Utility Boilers for Nitric Oxide Emission Reduction — Experience and Status Report," presented at AIChE 69th Annual Meeting, November 1976.

4-12 Crawford, A. R., et al., "The Effect of Combustion Modification on Pollutants and Equipment Performance of Power Generation Equipment," In: Proceedings of the Stationary Source Combustion Symposium, EPA-600/2-76-152c, June 1976.

4-13 Thompson, R. E., M. W. McElroy, and R. C. Carr, "Effectiveness of Gas Recirculation and Staged Combustion in Reducing NO_x on a 560 MW Coal-Fired Boiler," In: Proceedings of the NO_x Control Technology Seminar, EPRI Special Report SR-39, February 1976.

4-14 Selker, A. P., "Program for Reduction of NO_x from Tangential Coal-Fired Boilers, Phase II and IIa," EPA 650/2-73-005a and b, June 1975.

4-15 Hollinden, G. A., "NO_x Control at TVA Coal-Fired Steam Plants," Proceedings of Third National Symposium, ASME Air Pollution Control Division, April 24, 1973.

4-16 Crawford, A. R., et al., "Field Testing: Application of Combustion Modifications to Control NO_x Emissions from Utility Boilers," EPA-650/2-74-066, June 1974.

4-17 Selker, A. P. and R. L. Burrington, "Overfire Air Technology for Tangentially Fired Utility Boilers Burning Western U.S. Coal", Proceedings of the Second Stationary Source Combustion Symposium, Vol. II, Utility and Large Industrial Boilers, EPA 600/7-77-073b, July 1977.

4-18 Jain, L. K., et al., "State of the Art for Controlling NO_x Emissions, Part I: Utility Boilers," EPA-R2-72-072a, September 1972.

4-19 Hollinden, G. A., et al., "Evaluation of the Effects of Combustion Modifications in Controlling NO_x Emissions at TVA's Widow's Creek Steam Plant," EPRI SR-39, February 1976.

4-20 Friedrich, J. L., et al., "Nitrogen Oxides Reduction," Foster Wheeler Energy Corporation, EPRI SR-39, February 1976.

4-21 Ando, J., and H. Tohata, "NO_x Abatement for Stationary Sources in Japan," Environmental Protection Technology Series, EPA-600/2-76-013, January 1976.

4-22 Lyon, R. K., and J. P. Longwell, "Selective, Noncatalytic Reduction of NO_x with Ammonia," In: Proceedings of the NO_x Control Technology Seminar, EPRI Special Report SR-39, February 1976.

4-23 Muzio, L. J., J. K. Arand, and D. P. Teixeira, "Gas Phase Decomposition of Nitric Oxide in Combustion Products," In: Proceedings of the NO_x Control Technology Seminar, EPRI Special Report SR-39, February 1976.

4-24 Schreiber, R. J., et al., "Boiler Modification Cost Survey for Sulfur Oxides Control by Fuel Substitution," Environmental Protection Technology Series, EPA-650/2-74-123, November 1974.

4-25 Frendburg, A., "Performance Characteristics of Existing Utility Boilers When Fired with Low-Btu Gas," EPRI Conference Proceedings, Power Generation, Clean Fuels Today, April 1974.

4-26 Agosta, J. et al., "Status of Low Btu Gas as a Strategy for Power Station Emission Control," presented at the 65th Annual Meeting of the American Institute of Chemical Engineering, November 1972.

4-27 Martin, G. B., D. W. Pershing, and E. E. Berkau, "Effects of Fuel Additives on Air Pollutant Emissions from Distillate Oil-Fired Furnaces," EPA, Office of Air Programs AP-87, June 1971.

4-28 Shaw, H., "Reductions of Nitrogen Oxide Emissions from a Gas Turbine Combustor by Fuel Modification," ASME Trans., Journal of Engineering for Power, Vol. 95, No. 4, October 1973.

4-29 Kukin, I., "Additives Can Clean Up Oil-Fired Furnaces," Environmental Science and Technology, Vol. 2, No. 7, July 1973.

4-30 Bartok, W., et al., "Systems Study of Nitrogen Oxide Control Methods for Stationary Sources — Vol. II," prepared for National Air Pollution Control Administration, NTIS Report No. PB-192-789, Esso Research and Engineering, 1969.

4-31 Blakeslee, C. E., and A. P. Selker, "Program for the Reduction of NO_x from Tangential Coal-Fired Boilers, Phase I," Environmental Protection Technology Series, EPA-650/2-73-005, August 1973.

4-32 Kelley, D. V., data submitted at the EPRI NO_x Control Technology Seminar, San Francisco, by Pacific Gas and Electric Company, February 1976.

4-33 Letter from the Los Angeles Department of Water and Power to Acurex Corporation, May 5, 1975.

4-34 "Preliminary Environmental Assessment of Combustion Modification Techniques," Vol. II, EPA 600/7-77-119b, February 1977.

4-35 "Technology and Economics of Flue Gas NO_x Oxidation by Ozone," EPA 600/7-76-033, December 1976.

4-36 Kamo, R., et al., "The Effect of Air-Fuel Mixing on Recirculation in Combustion," Paper CP-62-12, API Research Conference on Distillate Fuel Consumption, June 1962.

4-37 Hegg, D. A., et al., "Reactions of Nitrogen Oxides, Ozone, and Sulfur in Power Plant Plumes," EPRI EA-270, September 1976.

4-38 Richards, J. and R. Gerstle, "Stationary Source Control Aspects of Ambient Sulfates: A Data Base Assessment," Pedco Final Report, EPA Contract No. 68-02-1321, Task 34, Pedco Environmental, Cincinnati, OH, February 1976.

4-39 Bennett, R. L., and K. T. Knapp, "Chemical Characterization of Particulate Emissions from Oil-Fired Power Plants," presented at the 4th National Conference on Energy and the Environment, Cincinnati, OH, October 1976.

4-40 Homolya, J. B., et al., "A Characterization of the Gaseous Sulfur Emissions from Coal and Coal-Fired Boilers," presented at the 4th National Conference on Energy and the Environment, Cincinnati, OH, October 1976.

4-41 Hall, R. E., CRB, IERL, U.S. EPA, personal communication.

4-42 Locklin, D. W., et al., "Design Trends and Operating Problems in Combustion Modifications of Industrial Boilers," NTIS PB235-712/AS, 1974.

4-43 Krippene, B. C., "Burner and Boiler Alterations for NO_x Control," Central States Section, The Combustion Institute, Madison, Wisconsin, March 1974.

4-44 Heap, M. P., et al., "Burner Design Principles for Minimum NO_x Emissions," EPA Coal Combustion Seminar, Research Triangle Park, North Carolina, EPA 650/273-021, June 1973.

4-45 Lyon, R. K., "Method for the Reduction of the Concentration of NO in Combustion Effluents Using Ammonia," U. S. Parent No. 3,900,554, assigned to Exxon Research and Engineering Company, Linden, New Jersey, August 1975.

4-46 Lyon, R. K. and J. P. Longwell, "Selective, Non-Catalytic Reduction of NO_x by NH_3," Proceedings of the NO_x Control Technology Seminar, EPRI SR-39, February 1976.

4-47 Campobenedetto, E. J., "The Dual Register Pulverized Coal Burner – Field Test Results," presented at Engineering Foundation Conference on Clean Combustion of Coal, Franklin Pierce College, New Hampshire, July 31-August 5, 1977.

4-48 Teixeria, D. P., "Status of Utility Application of Homogeneous NO_x Reduction," Proceedings of the NO_x Control Technology Seminar, EPRI SR-39, February 1976.

4-49 Cato, G. A., et al., "Field Testing: Applications of Combustion Modification to Control Pollutant Emissions from Industrial Boilers – Phase 1," Environmental Protection Technology Series, EPA-650/2-74-078-a,

4-50 Cato, G. A., et al., "Field Testing: Application of Combustion Modification to Control Pollutant Emissions from Industrial Boilers – Phase 2," Environmental Protection Technology Series, EPA-600/2-76-086a, April 1976.

4-51 Heap, M. P., et al., "Application of NO_x Control Techniques to Industrial Boilers," Ultrasystems, Inc., presented at the 69th Annual Meeting of the AIChE, Nov. 28 to Dec. 2, 1976.

4-52 Cichanowicz, J. E., et al., "Pollutant Control Techniques for Package Boilers, Phase I Hardware Modifications and Alternate Fuels," (Draft Report) Ultrasystems and Foster Wheeler, November 1976.

4-53 Maloney, K. L., "Western Coal Use in Industrial Boilers," Presented at the Meeting of the Western States Section of the Combustion Institute, Salt Lake City, Utah, April 1976.

4-54 Heap, M. P., et al., "Reduction of NO emissions from Package Boilers," Revised Draft Final Report by Ultra Systems, Inc., Irvine, California.

4-55 McGowin, C. R., "Stationary Internal Combustion Engines in the United States," EPA-R2-73-210, April 1973.

4-56 "Standard Support and Environmental Impact Statement — Stationary Reciprocating Internal Combustion Engines," (Draft Report). Acurex Corp./Aerotherm Division, Mountain View, California, Project 7152, March 1976.

4-57 Aerospace Corporation, "Assessment of the Applicability of Automotive Emission Control Technology to Stationary Engines," EPA-650/2-74-051, July 1974.

4-58 The American Society of Mechanical Engineers (ASME), "Power Costs, 1974 Report on Diesel and Gas Engines," March 1974.

4-59 Calspan Corporation, "Technical Evaluation of Emission Control Approaches and Economics of Emission Reduction Requirements for Vehicles Between 6000 and 14000 Pounds GVW," EPA-460/73-005, November 1973.

4-60 Bascom, R. C., et al., "Design Factors that Affect Diesel Emissions," SAE Paper 710484, July 1971.

4-61 Hills, F. J., et al., "CRC Correlation of Diesel Smokemeter Measurements," SAE Paper 690493, May 1969.

4-62 "Standards Support and Environmental Impact Statement, Volume I: Proposed Standards of Performance for Stationary Gas Turbines," EPA-450/2-77-017a, September 1977.

4-63 Shaw, H., "The Effects of Water, Pressure and Equivalence Ratio on Nitric Oxide Production in Gas Turbines," ASME Paper 73-WA/GT-1.

4-64 Hilt, M. B. and Johnson, R. H., "Nitric Oxide Abatement in Heavy Duty Gas Turbine Combustion by Means of Aerodynamic and Water Injection," ASME Paper 72-GT-53.

4-65 Stern, R. D., "The EPA Development Program for NO_x Flue Gas Treatment," In: Proceedings of the National Conference on Health, Environmental Effects, and Control Technology of Energy Use, EPA 600/7/76-002, February 1976.

SECTION 5

OTHER COMBUSTION PROCESSES

Significant amounts of the total fuels burned and NO_x emissions released in the United States are associated with small-scale combustion processes. These include important nonindustrial uses in domestic and commercial heating, hot water supply, a wide variety of incinerators, and open burning of solid wastes. The contribution to ambient NO_2 can be significant, particularly in localized, residential areas. Control techniques, costs, and energy and environmental impacts are discussed for those systems where data are available.

5.1 SPACE HEATING

Residential and commercial space heating generated about 1.1 Tg (1.2×10^6 tons) of NO_x during 1974, which accounts for approximately 9.0 percent of the total national stationary source NO_x emissions (see Section 2). Projections for nationwide emissions due to space heating have been made by the National Academy of Sciences (Reference 5-1). These projections, shown in Table 5-1, assume that approximately half of new housing units will use electricity for space heating. This assumption may be somewhat optimistic, from the standpoint of NO_x, due to the recent high rate of increase in the cost of electrical heat compared to oil or gas firing. The decline over the past 30 years in residential combustion, due to increased use of electrical heat, may reverse if electrical heating costs continue to increase faster than fuel costs.

Hall, et al. (Reference 5-2) studied the factors that affect emission levels from residential heaters. This project, which concentrated on an oil-fired warm air furnace, showed that excess air, residence time, flame retention devices, and maintenance are major factors in the control of emissions.

As shown in Figure 5-1, emissions of CO, HC, smoke, and particulates pass through a minimum as excess air is increased from stoichiometric conditions. By contrast, both thermal efficiency and NO emissions pass through maximum points as excess air is increased. The experimental results showed that increased residence time of the combustion products reduces emissions of CO, caseous HC, and smoke but has no effect on NO_x emissions. Combustion chamber material was found to affect all

TABLE 5-1. NATIONWIDE NO_x EMISSIONS FROM SPACE HEATING PROJECTED TO 1990 (REFERENCE 5-1)

Space Heating Sector	ANNUAL NO_x EMISSIONS (NO_2 Basis) Gg (10^6 tons)			
	1972	1980	1985	1990
Commercial	589 (0.65)	689 (0.76)	762 (0.84)	844 (0.93)
Residential	263 (0.29)	281 (0.31)	290 (0.32)	308 (0.34)
Total	852 (0.94)	970 (1.07)	1052 (1.16)	1152 (1.27)

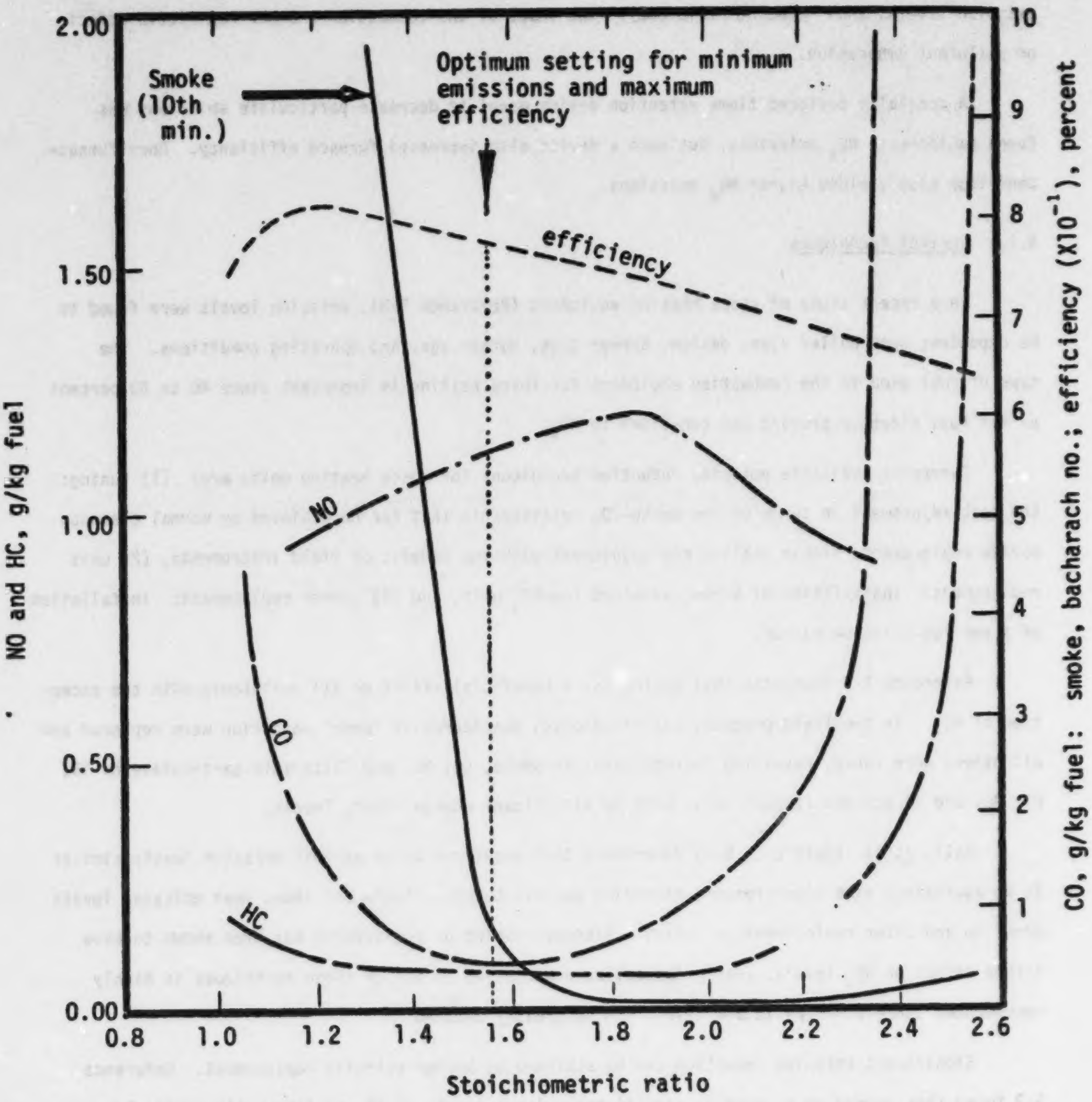


Figure 5-1. General trend of smoke, gaseous emissions, and efficiency versus stoichiometric ratio for residential heaters (Reference 5-4).

emissions. Furnaces with steel-lined chambers required higher excess air levels to reach optimum emission levels, thus reducing efficiency. The shape of the combustion chamber had little effect on pollutant generation.

A specially designed flame retention device meant to decrease particulate emissions was found to increase NO_x emissions, but such a device also increased furnace efficiency. Poor furnace condition also yielded higher NO_x emissions.

5.1.1 Control Techniques

In a recent study of space heating equipment (Reference 5-3), emission levels were found to be dependent upon boiler size, design, burner type, burner age, and operating conditions. The type of fuel used in the combustion equipment for space heating is important since 40 to 60 percent of the fuel nitrogen present was converted to NO_x.

Currently available emission reduction techniques for space heating units are: (1) tuning: the best adjustment in terms of the smoke-CO_2 relationship that can be achieved by normal cleanup, nozzle replacement, simple scaling and adjustment with the benefit of field instruments, (2) unit replacement: installation of a new, advanced low-NO_x unit, and (3) burner replacement: installation of a new low-emission burner.

Reference 5-3 indicates that tuning has a beneficial effect on all pollutants with the exception of NO_x. In the field program, oil-fired units considered in "poor" condition were replaced and all others were tuned, resulting in reductions in smoke, CO, HC, and filterable particulate by 59, 81, 90, and 24 percent respectively, with no significant change in NO_x levels.

Hall, et al. (Reference 5-4) determined that gas-fired units exhibit emission levels similar to an equivalent size high-pressure atomizing gun oil burner. Table 5-2 shows mean emission levels prior to and after replacement or tuning. Although tuning or replacement has been shown to have little effect on NO_x levels, yearly inspection accompanied by one of these techniques is highly recommended since other pollutant levels are so greatly reduced.

Significant emission reduction can be achieved by burner retrofit replacement. Reference 5-3 found this procedure to produce significantly lower levels of CO and filterable particulate. In general, recently developed burners have not demonstrated the ability to consistently reduce NO_x levels while many, in improving combustion efficiency and reducing emissions of other pollutants, actually increase NO_x emission over the standard burner.

TABLE 5-2. COMPARISON OF MEAN EMISSIONS FOR CYCLIC RUNS ON RESIDENTIAL OIL-FIRED UNITS (REFERENCE 5-3)

Units	Condition	Units in Sample	Mean Smoke No.	Mean Emission Factors kg/m^3 (lb/1000 gal)			
				CO	HC	NO$_x$	Filterable Particulate
All units	As Found	32	—	>2.65 (>22.1)	0.68 (5.7)	2.32 (19.4)	0.35 (2.9)
	Tuned	33	—	>1.96 (>16.4)	0.36 (3.0)	2.34 (19.5)	0.28 (2.3)
All units, except those in need of replacement	As Found	29	3.2	0.93 (7.8)	0.09 (0.72)	2.35 (19.6)	0.29 (2.4)
	Tuned	30	1.3	0.52 (4.3)	0.07 (0.57)	2.34 (19.5)	0.26 (2.2)

A number of commercially available burners were tested by Hall (Reference 5-2) wherein pollutant levels were determined under typical operation conditions. Combustion-improving devices yielded higher NO_x levels than the standard burner, but demonstrated a potential for reducing levels of one or more pollutants and improving combustion efficiency. Flame retention burners were shown to be capable of operating at low excess air levels, resulting in increased combustion efficiency with accompanied reduction in emission levels with the exception of NO_x.

An advanced residential warm air oil furnace has been developed in an EPA-funded program (References 5-5 and 5-6). The furnace is said to increase the fuel utilization efficiency by up to 10 percent. In addition, a 65 percent reduction in NO_x emission levels was realized.

The advanced oil furnace design consists of an optimized oil burner and firebox combination. The system has completed a 500 hour laboratory performance test. The tests evaluated the effects of combustion air swirl angle, nozzle spray angle, and axial injector placement on NO_x emissions levels for various oil flowrates and overall excess air combinations. The optimum burner was a nonretention gun-type with six swirl vanes set at a 26-degree angle. The firebox design selected was a cylindrical fin cooled firebox. The optimum burner/firebox combination yielded emissions of 0.6 g NO/kg of fuel (1.2 lb/ton) at 10 percent excess air compared to 2-3 g/kg (4-6 lb/ton) for the baseline commercial burners. Operation at these low excess air levels combined with use of outside air for combustion produced up to 10 percent increase in system efficiency (Reference 5-6).

In a related study, Combs and Okuda (Reference 5-7) investigated the commercial feasibility of an optimum low-NO_x distillate oil burner head. They reported that sheet metal stamping was the best fabrication method for commercial production of the burner head. They also investigated retrofit possibilities and found that the optimum burner heads were operationally satisfactory and had long life potential.

Emissions of NO_x from natural gas-fired furnaces were measured by the American Gas Association Laboratories (Reference 5-8). Measurements indicated that water-backed heat transfer systems emitted higher levels of NO_x compared to gas-to-air systems. Also, multiport burners emitted higher NO_x levels than single port burners. In another test, it was found that addition of a radiant screen placed above a water heater burner resulted in a net reduction of NO_x by about 55 percent.

Another advanced burner/furnace design is the "Blueray" system (Reference 5-9). This system consists of a "blue flame" oil burner integrated with the firebox of a warm air furnace package. Two sizes are currently available: 0.63 cm^3 oil/sec (0.6 gph), and 0.789 cm^3 oil/sec (0.75 gph). The efficiency of the burner is reported to be about 84 percent and the NO_x emission level is about 20 ppm. This is a significant improvement over conventional systems for which typical efficiencies are 75-80 percent, and NO_x emissions range from 70 to 90 ppm. In the Blueray system, combustion air and gases are recirculated throughout the combustion chamber; the recirculation zone is designed such that blue-flame burnout of CO and HC results. These systems are available as a single unit (burner/furnace combinations) for new installations. Retrofits to existing burners are not practical since the blue flame burner must be matched to the firebox geometry and heat transfer characteristics (Reference 5-10).

As an aid to control emission levels from residential and commercial space heating systems, the EPA has made available guidelines for oil burner adjustments (References 5-11, 5-12). The recommended adjustment procedures for residential systems apply to automatic oil burners used for heating one to three family dwellings. These guidelines are intended for the use of skilled technicians and for training service personnel. The recommended adjustment guidelines provide for efficient fuel utilization and minimize air pollution with reliable automatic operation. The adjustment procedures for commercial boilers apply to oil-fired cast iron firetube and watertube boilers.

5.1.2 Costs

The use of advanced, low-NO_x, burner-furnace units for new sales appears to be the most attractive option for NO_x control in space heating equipment. The Blueray unit has been commercially available since 1974 and has been widely tested in field installations. The Rocketdyne unit (Reference 5-5) is undergoing field demonstration preparatory to certification and potential commercialization. With proper maintenance, both units offer a NO_x reduction potential of 50 percent or greater compared to conventional units. Fuel savings of 5 percent of more, relative to standard units, are achievable with these units. Use of these low-NO_x units in new houses and for replacement of obsolete conventional units in existing installations would yield a nationwide decrease in residential NO_x emissions which would more than offset the potential emissions increase due to population growth for several decades.

The 1975 cost, less installation, of the Blueray unit was $550 (Reference 5-10). By contrast, the cost of conventional warm air furnaces ranges from $300-$500. The added cost of the low-NO_x unit may be justified, however, on the basis of the fuel savings resulting from the improved thermal efficiency. Cost data for the Rocketdyne unit are not yet available.

For long term application to NO_x control in new residential units, there is the additional possibility of utilizing the alternate design concept of catalytic combustion. This concept, discussed in Section 3.5, offers the potential for extremely low levels of NO_x (1-10 ppm) when firing natural gas or distillate oils. Catalytic combustion is still in the exploratory stage of development and no reliable cost estimates are available for residential heating systems.

The prospects for cost-effective NO_x control in existing space heating units are not promising. Furnace tuning and, if required, burner head replacement are strongly recommended for reduction of carbon monoxide and smoke and for improving unit efficiency. The impact on NO_x is negligible, however. Furnace tuning (cleaning, leak detection, sealing and burner adjustment) costs a minimum of $40 for the average residential unit. Burner head retrofit replacement costs an additional $25 less installation. These are usually cost effective in view of the fuel savings and increased safety derived from the maintenance.

5.1.3 Energy and Environmental Impact

5.1.3.1 Energy Impact

All three NO_x emission reduction techniques (tuning, unit replacement and burner replacement) result in improved system efficiencies and, consequently, reduced fuel consumption. The exact amount of improvement varies widely depending on the type of equipment. The most promising method, unit replacement, appears to offer in excess of 5 percent fuel savings. On a national basis, this represents a potential savings of 0.6 percent of annual fuel consumption if all space heating equipment were replaced with new designs.

5.1.3.2 Environmental Impact

The effect of lower excess air on CO, HC, and particulate emissions was discussed previously and is illustrated in Figure 5-1. By constraining incremental emissions during control development, however, it has been possible to achieve low-NO_x combustion conditions without adverse incremental emissions (Reference 5-6). Table 5-3 shows a comparison of typical uncontrolled units and a prototype unit with an optimized burner/firebox. Incremental emissions were held constant or reduced at the low-NO_x, high efficiency condition. Table 5-3 also shows incremental emissions with a commercially available oil emulsifier burner. Again, low NO_x operation was achieved with no adverse effects on incremental emissions (Reference 5-13).

Over 90 percent of residential and commercial warm air furnaces fire either natural gas or distillate oil. Emissions of sulfates and trace metals from these units are thus of minor concern compared to coal-fired boilers. About 3 percent of U.S. warm air furnaces still fire coal. For these, sulfates, trace metals and especially POM's could cause severe localized environmental

TABLE 5-3. EFFECT OF LOW-NO_x OPERATION ON INCREMENTAL EMISSIONS AND SYSTEM PERFORMANCE FOR RESIDENTIAL WARM AIR FURNACES

	Excess Air	Thermal Efficiency (Steady-State)	NO g/kg fuel	CO g/kg fuel	HC g/kg fuel	Smoke Bacharach
Typical uncontrolled field units (References 5-2,5-3)	90%	70%	1.1 - 2.7	1.05	0.1	3.2
Optimum low-NO_x unit (Reference 5-6)	15%	80%	0.6	1.0	0.1	1
Water/distillate oil emulsifier burner: (Reference 5-13)	32%	80%	0.85	0.3	--	~1

problems. However, it is doubtful that NO_x controls, except for fuel switching, will be developed and implemented for these sources, and they will not be considered further here.

An additional factor in evaluating incremental emissions for warm air furnaces is the cyclic nature of operation. Warm air furnaces typically undergo two to five on/off cycles per hour. Studies of emissions without NO_x controls show that the starting and stopping transients have a strong, sometimes dominant, effect on total emissions of CO, HC and particulate (smoke) (References 5-2 and 5-3). The effect of NO_x controls on transient emissions is presently unknown. Incremental steady-state emissions must eventually be weighed against the transient emissions for this significance to be shown.

Data on warm air furnace POM emissions under low-NO_x operation are apparently nonexistent. Data on both transient and steady operation with and without NO_x controls are needed to form a general conclusion on the total incremental impact of NO_x controls. Additionally, it should be emphasized that the incremental emissions data shown in Table 5-3 are for well maintained laboratory operation. Data are needed on long-term field operation with NO_x controls.

5.2 INCINERATION AND OPEN BURNING

5.2.1 Municipal and Industrial Incineration

According to a Public Health Service survey conducted in 1968 (Reference 5-14), an average of 2.5 kg (5.5 pounds) of refuse and garbage is collected per capita per day in the United States. An additional 2 kg (4.5 pounds) per capita per day are generated by incineration of industrial wastes, wastes burned in commercial and apartment house incinerators, and backyard burning. The total per capita waste generation rate is conservatively estimated at about 4.5 kg (10 pounds) per day (Reference 5-14).

Incineration is economically advantageous only if land is unavailable for sanitary landfill. Incineration requires a large capital investment, and operating costs are higher than for sanitary landfill.

The most common types of incinerators use a refractory-lined chamber with a grate upon which refuse is burned. Combustion products are formed by contact between underfire air and waste on the grates in the primary chamber. Additional air is admitted above the burning waste to promote burnout of the primary combustion products.

Incinerators are used in a variety of applications. The main ones are municipal and industrial solid waste management. Municipal incinerators consist of multiple chamber units that have capacities ranging from 23 kg (50 pounds) to 1,800 kg (4,000 pounds).

5.2.1.1 Emissions

Nationwide NO_x emissions from incineration in 1974 amounted to 39 Gg per year (43,400 tons per year) which is 0.3 percent of the total NO_x emissions from stationary sources. Fifty-five percent of these emissions result from industrial incineration with the remainder due to municipal incineration. A number of other multimedia effluents from incineration may be of greater concern than NO_x. These include metallic compounds in the particulate flyash and hopper ash and chlorinated organic and inorganic gaseous compounds. Incinerator effluent rates are strongly dependent on the composition of the solid waste, the incinerator design and specific operating variables such as excess air and firing rate. The effluent rates can vary considerably from day to day because of variations in refuse composition. An average emission factor for incineration of 1.5 g NO_2/ kg refuse (3 lb/ton) was reported by Niessen (Reference 5-15). AP-42 (Reference 5-16) specifies the same value for multichamber industrial and municipal incinerators. For single chamber industrial incinerators, a lower factor of 1 g NO_2/ kg refuse (2 lb/ton) is specified.

Stenberg, et al., conducted field tests to study the effects of excess combustion air on NO_x emissions from municipal incinerators (Reference 5-17). The nitrogen oxide emissions ranged from 0.7 g/kg (1.4 lb/ton) to 1.65 g/kg (3.3 lb/ton) of refuse charged for a 45.3 Mg (50 ton) per day batch-feed incinerator and a 227 Mg (250 ton) per day continuous-feed incinerator. As shown in Figure 5-2, NO_x emissions increase with increasing amounts of excess air. The amount of underfire air also has a significant effect on NO_x production and is shown in Figure 5-3.

In general, nitrogen oxide emissions from incineration are not a primary source of air pollution; however, particulate emissions are significant. It is for this reason that incinerator air pollution control equipment is adopted to the removal of particulate matter rather than NO_x. Activity in pollution abatement for incinerators to date has focused on particulate control rather than NO_x.

5.2.1.2 Control Techniques

The use of waste disposal methods other than combustion may be the most likely means for reducing NO_x emissions, since the methods normally used for control of other emissions from incineration, such as particulate matter, organics, and carbon monoxide, tend to increase emissions of

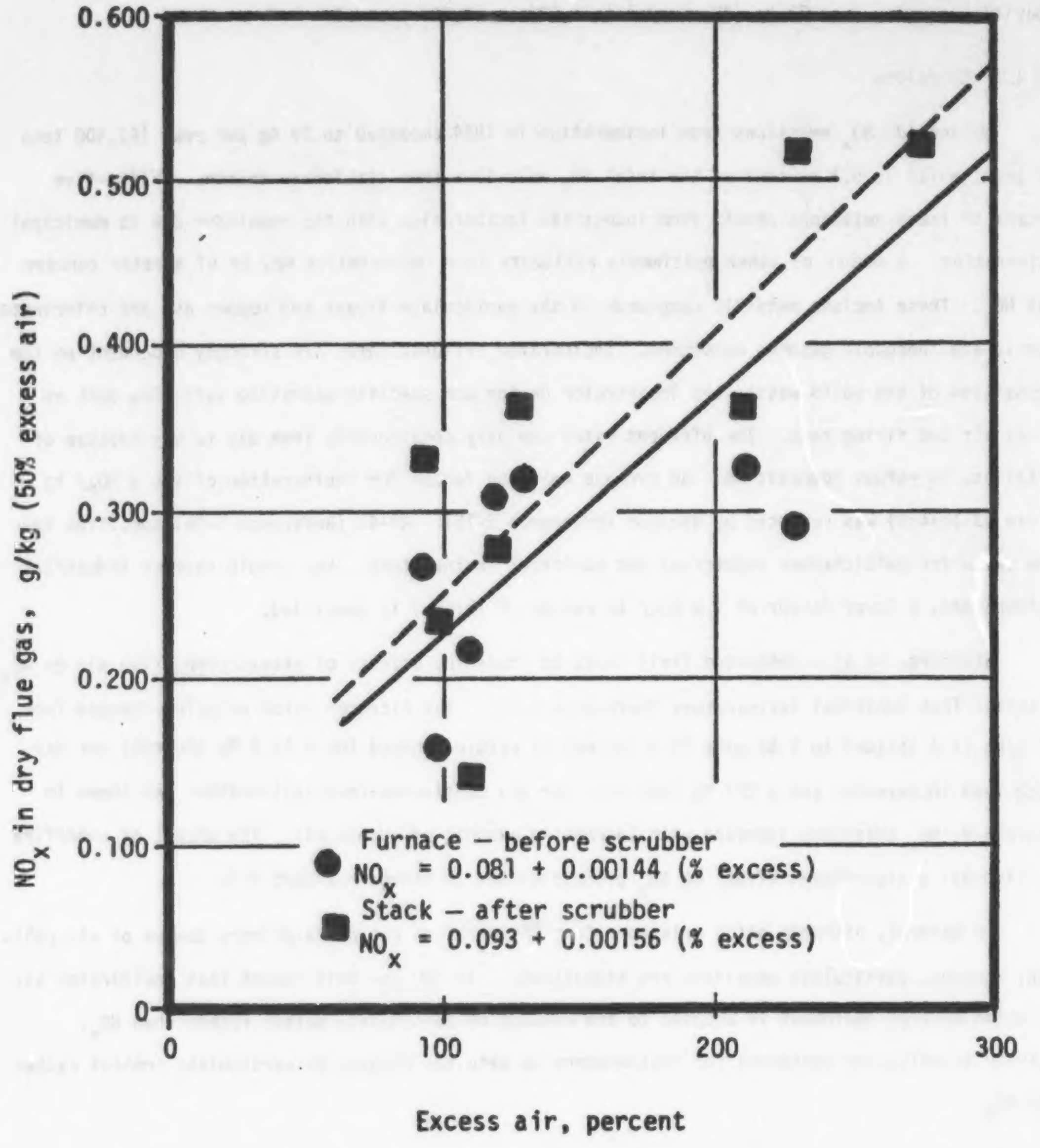


Figure 5-2. Effect of excess air on NO_x emissions from a 45.3 Mg (50 ton) per day batch-feed incinerator (Reference 5-17).

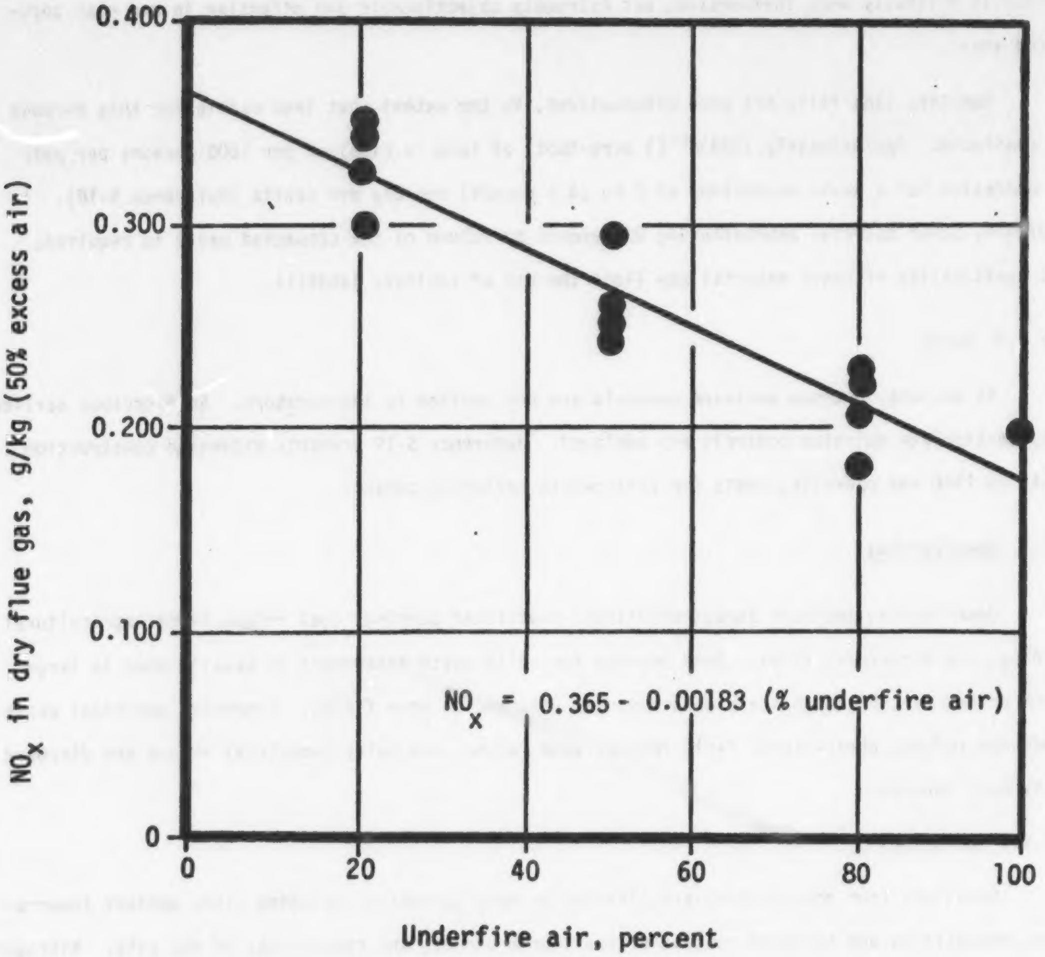


Figure 5-3. Effect of underfire air on NO_x emissions from a 227 Mg (250 ton) per day continuous-feed incinerator (Reference 5-17).

NO_x. Other disposal methods include dumping, sanitary landfill, composting, burial at sea, disposal in sewers and hog feeding.

One of the first refuse disposal methods used was open dumping of refuse on land. This method is obviously very inexpensive, but extremely objectionable and offensive in and near populated areas.

Sanitary land fills are good alternatives, to the extent that land usable for this purpose is available. Approximately 1233 m^3 (1 acre-foot) of land is required per 1000 persons per year of operation for a waste production of 2 kg (4.5 pounds) per day per capita (Reference 5-18). In addition, cover material approximating 20 percent by volume of the compacted waste is required; the availability of cover material may limit the use of sanitary landfill.

5.2.1.3 Costs

At present, gaseous emission controls are not applied to incinerators. As described earlier, only particulate emission controls are employed. Reference 5-19 presents estimated construction costs in 1966 and operating costs for particulate pollution control.

5.2.2 Open Burning

Open burning includes forest wildfires, prescribed burning, coal refuse fires, agricultural burning, and structural fires. Open burning for solid waste management is usually done in large drums or baskets, in large-scale open dumps or pits and on open fields. Commonly, municipal waste, landscape refuse, agricultural field refuse, wood refuse, and bulky industrial refuse are disposed of by open burning.

5.2.2.1 Emissions

Emissions from open burning are affected by many variables including wind, ambient temperature, composition and moisture content of the debris burned, and compactness of the pile. Nitrogen oxides emissions depend mainly upon the nitrogen content of the refuse. Generally, due to the low temperatures associated with open burning, nitrogen oxides emissions are low.

Annual emissions from open burning vary from year to year, and the data for the various sources are not entirely consistent. Table 5-4 shows the estimated NO_x emissions from open burning sources for 1971 as reported in Reference 5-20. More recent estimates from the 1976 NEDS data file and Reference 5-21 are also given in Table 5-4. Increasing awareness of air pollution problems has contributed to a general decline in the quantity burned (and thus the emissions) from those categories which can be controlled. For example, despite the continuing growth in crop harvest, NO_x emissions from agricultural open burning has declined from an estimated 29 Gg (32,000 tons) in 1969 to 13 Gg (14,300 tons) for 1973 (Reference 5-21).

TABLE 5-4. ANNUAL EMISSIONS OF NITROGEN OXIDES FROM OPEN BURNING

Source	NO_x Emissions			
	1971, Reference 5-20		1976 NEDS	
	Gg	10^3 Tons	Gg	10^3 Tons
Solid Waste Disposal	150	165	95	105
Forest Wildfires	138	152	48	53
Prescribed Burning	19	21	30	33
Agricultural Burning	29	32	13[a]	14[a]
Coal Refuse Fires	31	34	53	58
Structural Fires	6	7	5	6

[a] 1973 estimate from Reference 5-21.

5.2.2.2 Control Techniques

Solid Waste Disposal

From the standpoint of air pollution, sanitary landfills are good alternatives to open burning. In addition to the land necessary for sanitary landfill, cover material approximating 20 percent by volume of the compact waste is required. The availability of cover material may limit the use of the sanitary landfill method.

Unusual local community factors may lead to unique approaches to the landfill site problem. For example, Reference 5-22 reports that in a pilot project the refuse is shredded and baled for loading on rail cars for shipment to abandoned strip mine landfill sites.

Other noncombustion alternatives may have application in some localities. Composting is now being tested on a practical scale (Reference 5-23). Hog feeding has been used for disposal of garbage. Dumping at sea has been practiced by some seacoast cities, but is now extensively regulated.

Elsewhere, refuse has been ground and compressed into bales, which are then wrapped in chicken wire and coated with asphalt. The high-density bales sink to the bottom in the deeper ocean areas and remain intact. The practice of grinding garbage in kitchen units and flushing it down the sewer has been increasing. This in turn increases the load of sewage disposal plants and the amount of sewage sludge (Reference 5-24).

Forest Wildfires

In the United States, forests comprise approximately 3.2 x $10^{12} m^2$ (786 million acres), or 34.4 percent, of the land area. Seasonal forest fires are quite prevalent in dry western regions. Considerable activity has been and is being directed toward reducing the frequency of occurrence and the severity of these fires. These activities include publishing and advertising information on fire prevention and control, surveillance of forest areas where fires are likely to occur, and various firefighting and control activities. Additionally, prescribed burning is being used to reduce the loading of combustible underbrush and thereby decrease the fire hazard and potential fire spread rate.

The U.S. Forest Service estimated that 2.06 x $10^{10} m^2$ (5.11 million acres) of land were burned in 1976 (the World Almanac, 1978). A similar estimate for 1971 (Reference 5-20) was 1.73 x $10^{10} m^2$ (4.28 million acres) burned, producing 138 Gg (152,000 tons) of nitric oxides emissions. Emissions from forest fires are dependent on the local combustion intensity, the overall scale of the fire, and, to some extent, the nitrogen content of the fuel. These in turn are related to the topography of the forest, the composition and dryness of the underbrush, the local meteorological conditions, and the elapsed time since a previous fire. The topography of the forest, the composition and dryness of the underbrush, the elapsed time since a previous fire and the meteorological condition are all interrelated and dictate the burn rate and spread, intensity of the burn, and the size of the burn.

Prescribed Burning

Prescribed burning is the use of controlled fires in forests and on ranges to reduce the possibility of wildfire and for other land management goals. Four classes of open burning operations are traditionally practiced by the Forest Service (Reference 5-25):

- Slash disposal resulting from forest harvesting operations
- Forest management operations for forest floor fuel reduction, seedbed preparation, pest control, forest thinning and undergrowth control
- Public works construction operations to clear reservoir and dam-sites, utility and highway rights-of-way and building and structure site areas

- Public works maintenance operations for the disposal of reservoir driftwood and of rights of way and storm damage debris

In addition, controlled burning is used to reduce unwanted quantities of waste and to improve land utilization.

Because collection and incineration of these materials would tend to increase NO_x emissions, the only current way to control emissions is to avoid combustion. In the future it may be possible to develop incineration processes that can control NO_x and other emissions such as particulate matter, organics, odorous compounds, and carbon monoxide; or it may be possible to develop equipment that can burn these materials as substitutes for fossil fuels.

Other alternatives to incineration are abandonment or burying at the site, transport to and disposal in remote areas, and utilization. Abandonment or burning at the site is practical in cases where no other harmful effects will ensue. Abandoned or buried vegetation can have harmful effects upon plant life by hosting harmful insects or organisms, for example. Agricultural agencies such as the U.S. Department of Agriculture, or state and local agencies should be consulted before these techniques are employed.

Agricultural Burning

Agricultural burning includes the burning of residues of field crops, row crops, and fruit and nut copes for at least one of the following reasons (Reference 5-21):

- Removal and disposal of residue at low cost
- Preparation of farmlands for cultivation
- Clearing to facilitate harvest
- Control of disease, weeds, insects, or rodents

Mitigation of the environmental impact of agricultural open burning is possible by proper fire and fuel management (for example, single-line backfiring), meteorologically scheduled burning to optimize dispersion, or by the substitution of other alternatives, such as mobile incineration, incorporation into the soil, and mechanical removal. Care must be exercised in the choice of alternate methods of disposal since a change in method may have significant adverse effects. For example, *in situ* burning can provide thermal treatment to the soil which raises the production yield substantially, incorporation of the residue into the soil may restrict rapid replanting, and residue decomposition may deplete the soil nitrogen.

Coal Refuse Fires

An estimated 53 Gg (58,000 tons) of NO_x is emitted each year from burning coal refuse. Extinguishing and preventing these fires are the techniques used for eliminating these emissions.

These techniques involve cooling and repiling the refuse, sealing refuse with impervious material, injecting slurries of noncombustibles into the refuse, minimizing the quantity of combustibles in refuse, and preventing ignition of refuse. The NO_x emissions from coal refuse fires are highly dependent on the nitrogen content of the coal.

Structural Fires

There were almost one million buildings attacked by fire during 1971 with losses estimated at $2.21 billion (Reference 5-20). An estimated 6.3 Gg (7,000 tons) of NO_x were emitted during 1971. Prevention is the best control technique to reduce these emissions. Use of fireproof construction, proper handling, storage, and packaging of flammable materials, and publishing and advertising information on fire prevention are some of the techniques used to prevent structural fires.

Fire control techniques include the various methods for promptly extinguishing fires: use of sprinkler, foam, and inert gas systems; provision of adequate firefighting facilities and personnel; provision of adequate alarm systems. Information on these and other techniques for prevention and control are available from agencies such as local fire departments, National Fire Protection Association, National Safety Council, and insurance companies.

5.3 INDUSTRIAL PROCESS HEATING

Fossil fuel derived heat for industrial processes is supplied in two ways: (1) by direct contact of the raw process material to flames or combustion products in furnaces or specially-designed vessels, and (2) by heat transfer media (e.g., steam, glycol or hot water) from boilers and I.C. engines. NO_x emissions and control techniques for the latter equipment types have been described in previous sections of this document. The former equipment types are described in the present section. Industries covered include petroleum and natural gas, metallurgical, glass, cement, and coal preparation plants. Much of this section is taken directly from a recent study of industrial process heating performed by the Institute of Gas Technology (Reference 5-28).

There is currently very little application of NO_x control to industrial process heating equipment. Consequently there are very few data on NO_x control costs or energy and environmental impact, and separate sections for these topics will not be included. EPA's Industrial Environmental Research Laboratory (RTP) is sponsoring a field test program to identify the potential for NO_x control in a diversity of process furnaces, ovens, kilns, and heaters. Partial results from that study are given in Reference 5-26 and are discussed, as appropriate, in the following subsections. The complete results of that program (scheduled for 1978) will provide a broad data base on which to evaluate alternate control options.

5.3.1 Petroleum and Natural Gas

5.3.1.1 Process Description

Oil and gas production, gas plants, and pipeline stations are usually located in remote areas far from population centers. Emissions do not, therefore, contribute substantially to ambient NO_2 levels in populous areas. Petroleum refineries, however, are often located in or near densely populated areas.

Petroleum refining is the process of converting crude oil into salable products. Crude oil is charged to an atmospheric pipestill where light products are separated and taken overhead and light catalytic reforming feed, raw gasoline, kerosene, middle distillate, and heavy gas oil are taken as sidestream products. The reduced crude is charged to a vacuum pipestill where heavy gas oil, lube stocks, and residuum are cut.

Atmospheric and vacuum gas oils are charged to catalytic cracking units, which provide light ends, cracked gasoline, and fractions for blending distillate and residual fuels. Reduced crude is used in making asphalt or residual fuels, and is often fed to coking units to increase the yield of distillate products. Catalytic cracking and coking produce propylene and butylene, which are often alkylated with isobutane to make alkylate. Sometimes the olefins are polymerized for gasoline or chemical production. Catalytic reforming increases the octane number of naphtha by converting naphthenes (saturated cyclic hydrocarbons) and paraffins to aromatics. Hydrogen treating is used to reduce sulfur content, increase stability, and improve burning characteristics of kerosenes and middle distillates.

The relative volumes of gasoline, kerosene, middle distillate, heavy fuel oil, etc., can be adjusted by diverting heavy gasoline fractions from gasoline to middle distillate and cat-cracking feed, by diverting coker feed to heavy fuel, and by other changes.

A fluid-bed catalytic-cracking unit is often the heart of a modern refinery. Preheated gas oil is charged to a moving stream of hot regenerated catalyst while it is being transferred from the regenerator to the reactor. The gas oil is cracked in the reactor or the tube inlets to the reactor; the products then pass through cyclone separators for removal of entrained catalyst and are cut into products in a fractionator. Coke forms on the catalyst during the reaction.

Spent catalyst is withdrawn from the bottom of the reactor and transferred to the regenerator where coke is burned off. The regenerator flue gas passes through cyclone separators for catalyst removal and is discharged through the stack. The hot, regenerated catalyst flows back to the reactor, supplying heat and catalyzing the cracking reaction.

The regenerator flue gas contains about 10 percent carbon monoxide. This gas is sometimes fed to a CO boiler where it is burned in preheated air to generate steam. Auxiliary fuel is required to maintain satisfactory combustion conditions.

Typical refinery process heaters are the cabin-type furnace, used for heat release rates above 44 MW (150 x 10^6 Btu/hr), and the vertical cylindrical furnace, used for heat duties below 23 MW (80 x 10^6 Btu/hr). Either type may be used in the 23 to 44 MW (80 to 150 x 10^6 Btu/hr) range. Combustion boxes are lined with refractory. Fuels may be liquid, gas, or a combination of both. Gas burners operate with 10 to 40 percent excess air, liquid burners with 20 to 80 percent. Stack temperatures are 478K to 756K (400F to 900F).

5.3.1.2 Emissions and Control Techniques

Process Heaters

Oxides of nitrogen emissions in the petroleum and natural gas industries result from the combustion of fuel in process heaters and boilers, and from internal combustion engines used to drive compressors and electric generators. Annual NO_x emissions for 1974 from petroleum process heaters are estimated to be 147 Gg (162,000 tons). NO_x control techniques for these sources are described in Section 4.2.1 of this report.

Recent test data (Reference 5-26) on NO_x emissions from both natural draft and mechanical draft heaters are summarized in Table 5-5. Five vertically fired natural draft heaters ranging in size from 11 to 26 MW (36 to 87 x 10^6 Btu/hr) were tested. These units had 10 to 32 burners sized about 940 ± 140 kW. Baseline NO_x emission factors, which were in agreement with the findings of Bartz (Reference 5-27), ranged from 39 to 52 ng/J (90 to 120 lb/10^9 Btu), considerably lower than the EPA emission factor for this category of 95 ng/J (220 lb/10^9 Btu). Combustion modifications for these tests included fuel heat content variation, load variation, burner air register adjustment and BOOS.

Prior work by Bartz (Reference 5-27) had attributed large changes in NO_x emissions to fluctuations in fuel gas composition. However, the tests reported in Reference 5-26 indicate that NO_x does increase with increased fuel heating value, although not to a significant degree. The results are not conclusive, and more tests with different heaters and a wider variation in heating value are needed.

Two of the natural draft heaters were tested during process rate changes of ±20 percent. Figure 5-4 shows the observed decrease in NO_x emissions as the load is increased. The probable cause for the NO_x reduction is that excess air was reduced as the load was increased.

TABLE 5-5. EFFECTS OF NO_x CONTROLS ON NO_x EMISSIONS FROM PETROLEUM PROCESS HEATERS (REFERENCE 5-26)

Device Type	Fuel	Average Baseline NO_x		Maximum Percent Reduction in NO_x	Combustion Modification
		ng/J	ppm @ 3% O_2		
Natural Draft Process Heater	Ref. Gas[a]	59	116	18	4/32 BOOS
Natural Draft Process Heater	Ref. Gas	50	97	22	Air Register Adjust
Natural Draft Process Heater	Ref. Gas	39	76	21	High Load, Low O_2
Natural Draft Process Heater	Ref. Gas	52	103	8	2/16 BOOS
Natural Draft Process Heater	Ref. Gas	49	98	24	Air Register Adjust
Forced Draft Heater, Air Preheat	Ref. Gas	163	320	0	Baseline Lowest O_2
	No. 6 Oil	113	222	0	Low O_2 No Effect
Forced Draft Heater	Ref. Gas	109	214	67	Low O_2
	No. 6 Oil	88	157	8	Low O_2

[a] Refinery gas

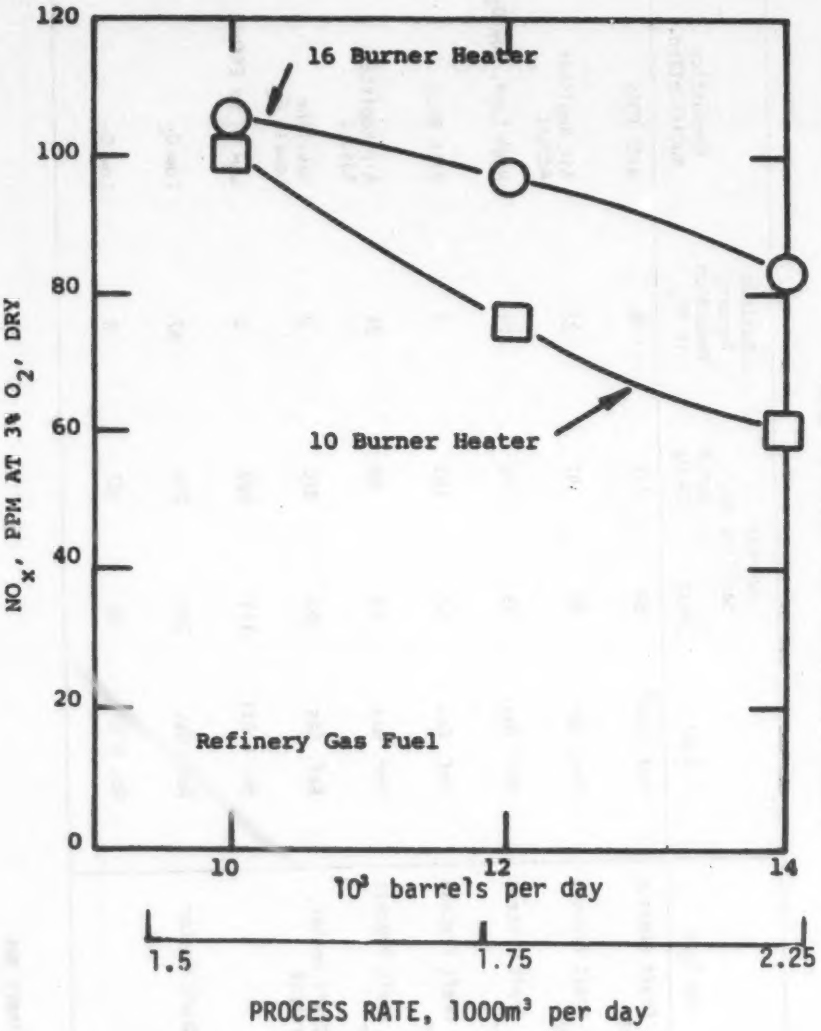


Figure 5-4. Effect of process rate on NO$_x$ emissions from a process heater (Reference 5-26).

Staged combustion for NO_x control was attempted by adjusting the air registers and taking burners out of service. Although NO_x emissions were reduced (see Table 5-5), the natural draft heaters did not respond to burner adjustments as well as expected, based on previous results with other types of boilers. There are three primary reasons for this. First, in most cases the burner removal patterns resulted in increased excess air which could not be lowered to baseline levels because of furnace pressure limits. Secondly, the design of natural draft burners utilizes the fuel flow as an aid to induce combustion air. This acts to defeat the attempt to achieve staged combustion. Finally, the in-line vertically-fired burner arrangement used for most heaters does not provide much inter-burner mixing, a necessary feature of staged combustion.

Two mechanical draft heaters, one with air preheat, were tested while firing either process gas or Number 6 fuel oil. Both were vertical cylindrical types and had only one burner; therefore, the only possible combustion modification was variation of excess air. As shown in Table 5-5, the unit with air preheat and higher emissions for both oil and gas firing. For both units, changes in excess air had little effect on NO_x emissions when firing oil. For the unit without air preheat, reductions in NO_x from 64 ng/J to 36 ng/J were achieved in one test with refinery gas when the excess oxygen was reduced from 5 percent to 2 percent.

Catalytic Crackers and CO Boilers

NO_x is also released from the catalytic-cracking regenerator and from CO boilers, which are fired by the catalytic cracker off gas. Emission testing in CO boiler stacks, summarized in Table 5-6, has shown results ranging from 100 ppm to 230 ppm of NO_x. Hunter (Reference 5-26) reported testing one CO boiler that was equipped with staged air ports. Baseline emissions were 126 ppm. Lowering excess oxygen from 2.1 to 1.8 percent reduced NO_x by 8 percent. Adjustment of the air ports and BOOS had negligible effect on NO_x emissions. CO emissions, however, were very sensitive to excess air and increased rapidly below about 2 percent excess oxygen. The lack of response of NO_x to combustion modifications is attributed to NO_x that is formed from ammonia in the CO gas feed acting similarly to fuel nitrogen in oil or coal.

The average emission factor for NO_x from fluid catalytic cracking units is estimated in Reference 5-16 as 0.24 kg NO_2/liter feed (84.0 lb/10^3 bbl feed). The total nationwide annual emissions from fluid bed and thermal cat crackers is estimated in Section 2 to be 45 Gg (50,000 tons) in 1974. If the regenerator exhaust is burned in a CO boiler, the resulting NO_x emissions can presumably be controlled by the classical methods discussed in Section 4.2.1 of this report.

TABLE 5-6. NO_x EMISSIONS FROM PETROLEUM REFINERY CO BOILERS (REFERENCE 5-28)

Investigator	NO_x (ppm as measured)
Schulz, et. al., (Reference 5-29)	104-116 (average 106)
Schulz, et. al., (Reference 5-30)	70-89 (average 78)
Shea (Reference 5-33)	96-233 (average 163)
Shea (Reference 5-31)	101-159 (average 135)
Cowherd (Reference 5-32)	108-162 (average 129)

5.3.2 Metallurgical Processes

5.3.2.1 Process Description and Control Techniques

The iron and steel industry is the predominant source of NO_x emissions derived from metallurgical processes. Other industries, such as aluminum production, extensively use electric melting furnaces or operate the process equipment at temperatures below the minimum required for formation of significant quantities of NO_x. Copper, lead, and zinc smelting require combustion operation in the reverberatory furnaces and converters (copper) and in sintering machines (lead and zinc). These combustion emissions are deemed insignificant relative to the emissions from the iron and steel industry. Emissions from these other industries may become significant as a result of the trend toward higher melting rates in new equipment designs. This section reviews the equipment types and available NO_x control technology for the major sources of NO_x within the iron and steel industry. Section 5.3.2.2 summarizes NO_x emission factors for these equipment types. Major portions of this section are taken from a 1976 IGT study (Reference 5-28) which uses 1971 steel industry data as a source for fuel consumption and NO_x emissions estimates.

Pelletizing

Pelletizing of extremely fine low grade iron ore occurs in a specially designed furnace at or near the iron mine. The cost of shipping the unbeneficiated ore would be almost double that of the pelletized product.

Previous studies by the Institute of Gas Technology have shown that pelletized ore production will be about 54 Tg per year (60 million tons/yr) by 1985. The fuel consumed by the pelletizing furnaces has remained about constant at 0.7 MJ/kg (600,000 Btu/ton). This indicates that annual NO_x emissions from pelletizing furnaces will reach about 7.65 Gg (8,500 tons) by 1985. The steel industry and equipment builders are considering coal firing the pelletizing furnace combustion chambers. If this is done, it will probably bring about an increase of about 50 percent in NO_x emissions. There is no information available concerning NO_x control techniques for pelletizing furnaces (Reference 5-28).

Sintering

Some of the iron ore and flue dusts are available in particle sizes too small to be charged directly to the blast furnace. These particles are mixed with flux and coke breeze and loaded onto a traveling grate-sintering machine. An auxiliary fuel such as natural gas, coke oven gas, or oil is used to initiate combustion on the surface of the mixture and is referred to as ignition fuel. Combustion is continued over the length of travel by forcing air through the mixture on the grates.

The mixture is heated to a fusion temperature, which causes agglomeration of the iron-bearing particles. The discharged sinter is cooled, crushed, and screened prior to transfer to the blast furnace charging oven.

The major source of energy used in the production of sinter is the carbon content of coke breeze and flue dust. The amount of ignition fuel required is about 140 J/g (0.12 million Btu per ton) of sinter. The total fuel requirement, including coke breeze, is about 1.74 kJ/g (1.5 million Btu per ton) of sinter.

The use of sinter machines to agglomerate ore fines, flue dust, and coke breeze has been declining since 1966 and amounted to 39 Tg (43×10^6 tons) in 1971. If the present rate of decline continues, the 1985 production of sinter would be about 24.3 Tg (27×10^6 tons). The attitude of the steel industry is mixed because many steel plants are phasing out sinter lines, while at least one major producer has replaced several small sinter lines with a large machine designed to meet pollution control regulations. On the other hand, the use of sintering for recycling iron has simultaneously been increasing. Therefore, the projected decrease in the number of sinter machines may not occur. In any case, the IGT estimates (Reference 5-28) show that NO_x will continue to be a major pollutant. There is no information available concerning NO_x emission control techniques for these furnaces.

Blast Furnace

The blast furnace is the central unit in which iron ore is reduced, in the presence of coke and limestone, for the production of pig iron. The blast furnace itself is normally a closed unit and therefore has no atmospheric emission. A preheated air blast is supplied to the furnace from the blast furnace stove, through nozzle-like openings called tuyeres, The subsequent reactions in the blast furnace are not pertinent to this discussion. Excellent descriptions are available, however, such as the complete discussion of the process of changing raw ore to finished steel published by the United States Steel Corporation (Reference 5-34).

The hot blast reacts with the coke to produce heat and more carbon monoxide than is needed to reduce the ore. The excess CO leaves the top of the blast furnace with other gaseous products and particulates and is known as blast furnace gas. This gas is cleaned to remove the particulates, which could later cause plugging. It is then available for heating purposes. Blast furnace gas contains about one percent hydrogen and 27 percent carbon monoxide; it has a heating value of approximately 3600 kJ/Nm^3, or, 92 Btu/ft^3 (Reference 5-34).

Coke Ovens

Coke is an essential component in making pig iron and steel; coke ovens are generally an integral part of the steel plant complex. One-sixth of the total bituminous coal produced is charged to coke ovens. On the average, 1.4 kg of coal is required for each kilogram of coke produced.

Conventional coking is done in long rows of slot-type ovens into which coal is charged through holes in the top of the ovens. The sidewalls, or liners, are built of silica brick, and the spaces between the chambers are flues in which fuel gas burns to supply the required heat. Each kilogram of coal carbonized requires 480 to 550 kJ (450 to 520 Btu). Flue temperatures are as high as 1,753K or 2,700F (Reference 5-35). Much of the remaining heat in the partially spent combustion gases is accumulated in a brick checkerwork, which releases it to preheat the combustion air when the cycle is reversed. This is a typical regenerative cycle to conserve fuel and give a higher flame temperature.

The coal in the coking chambers undergoes destructive distillation during a heating period of about 16 hours. The noncondensable gaseous product is known as coke oven gas and on a dry basis has a heating value of about 22 MJ/Nm^3 (570 Btu/ft^3). Approximately 35 percent of the coke oven gas produced is used in heating the oven.

The major sources of emissions from coke ovens are the rapid evolution of steam and other gases when moist coal is charged, the discharge of gases and particulates from the charging openings during charging, and the emissions during the coke push and subsequent quencing. Recent coke-oven battery designs have reduced the emissions from charging and pushing by using advanced engineering features and improved operating procedures. During the coking process, leakage from the push side and coke side door seals can account for most of the emissions during the coking process itself. Improved door sealing techniques reduce door leakage substantially.

Although the current practice of firing coke ovens with a mixture of blast furnace gas and coke-oven gas and slow mixing in the combustion chambers should tend to minimize NO_x production, the estimated total is substantial because of the large quantity of fuel consumed.

The reduction in the coke required per kilogram of hot metal achieved during the 1960's will continue, but steel mills are currently installing new coke ovens because of the increased need for hot metal due to the high BOF* hot metal-scrap ratio. It is believed that the decline in coke rate may have been stopped by the increased cost of fossil fuels used as injectants. The 1985 projection for coke-oven underfiring fuel is 485 PJ (458 trillion Btu). If the NO_x concentration remains constant, the resulting total emissions of NO_x will reach 57.8 Gg (64,120 tons) per year.

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*Basic Oxygen Furnace

Although it may be reasonable to assume that substitution of form coke may result in a substantial reduction in NO_x production, the general opinion in the steel industry is that form coke will not be a significant factor in 1985 (Reference 5-28).

Blast Furnace Stove

Between 2.2 and 3.5 kg of blast furnace gas is generated for each kilogram of pig iron produced. Some 18 to 24 percent of this gas is used as fuel to heat the three stoves which are usually associated with each blast furnace. Two are generally on heat while the third is on blast.

The blast furnace stove is a structure about 8 to 8.5 m (26 to 28 feet) in diameter and about 36 m (120 feet) high. A roughly cylindrical combustion chamber extends to the top of the structure and the hot combustion gases pass through a brick checkerwork to the bottom by reverse flow and then to the stack. The checkerwork usually contains 25,500 m^2 (275,000 ft^2) of heating surface and has about 85 percent thermal efficiency. Unlike the conventional regenerators, which extract heat from the waste combustion gases, the blast furnace stove is heated by burning fuel. The stored heat is then used to preheat air for the combustion of fuel in the furnace to be served.

As in the case of coke oven underfiring, the blast stoves require very large quantities of fuel for heating. However, since the stoves are heated primarily with blast-furnace gas (3.0 to 3.5 MJ/Nm^3, or 80 to 95 Btu/ft^3) the NO_x concentration is lower due to the presence of diluents and a low flame temperature.

The projected need for hot metal in 1985 is 112 Tg (124 million tons). This amount of hot metal will require 295 PJ (280 trillion Btu) for blast-stove heating. Assuming no reduction in NO_x stack-gas concentration, the NO_x emission in 1985 will be 17.7 Gg/yr (19,600 tons/yr). Because of the low estimated NO_x concentration and the presence of inerts in the fuel gas, equivalent to flue-gas recirculation, the potential for NO_x reduction is probably small (Reference 5-28).

Open Hearth Furnace

Steel making by the open hearth process has been decreasing since it reached a peak in 1956, when it represented 90 percent, or 92.7 Tg (103 million tons), of the total production. The use of open hearth furnaces is expected to continue to decline and will probably amount to about 10 percent of total steel production by 1985. Regardless of this dramatic decline due to the inroads of the basic oxygen furnace (BOF) and electric arc furnace steelmaking processes, its NO_x emission potential deserves consideration.

The open hearth furnace is both reverberatory and regenerative, like the glass melting furnaces. It is reverberatory in that the charge is melted in a shallow hearth by heat from a flame passing over the charge and by radiation from the heated dome. It is regenerative in that the remaining heat in the partially spent combustion gases from the reverberatory chamber is accumulated in a brick filled chamber, or "checker", and released to preheat the incoming combustion air when the cycle is reversed. Fuel of low calorific value such as blast furnace gas as well as the combustion air may be preheated by the checkers in order to obtain the high temperatures required.

Hot metal from the blast furnace, pig iron, scrap iron, and lime are the usual materials charged to an open hearth furnace. These are heated over a period averaging 10 hours, at a temperature as high as the refractories will permit. Fuel oil is the preferred fuel and is burned with excess air to provide an oxidizing influence on the charge.

NO_x emissions from open hearth furnaces are very high because of the high combustion air preheat temperature, high operating temperature, and the use of oxygen lances to increase production rates. The data available indicate that NO_x concentrations will be in the 1000 to 2000-ppm range. Although many open hearths are being phased out because of emission control difficulties and better economics of steel production with the BOF process, several steel mills are modernizing open hearth shops, including pollution control equipment to provide flexibility in the hot metal-scrap ratio, particularly those mills with a hot-metal deficiency. Therefore, predictions that the open hearths will be phased on entirely by 1985 are unrealistic, and it is anticipated that about 13.5 Pg (15 million tons) will still be made by the open hearth process in 1985. Fuel consumption has been decreasing and may reach 2.9 MJ/kg (2.5 million Btu/ton) in 1985. This will require a fuel consumption of 40 PJ (37.5 trillion Btu) for open hearth steel production and result in an NO_x emission level of 14 Gg (15,750 tons) (Reference 5-28).

Basic Oxygen Furnace

In the basic oxygen furnace (BOF), oxygen is blown downward through a water-cooled lance into a bath containing scrap and hot metal. Heat produced by oxidation of carbon, silicon, manganese, and phosphorous is sufficient to bring the metal to pouring temperature and auxiliary fuel is not required. The furnace is an open top, tiltable, refractory-lined vessel shaped somewhat like the old-fashioned glass milk bottle. Furnace capacities range up to 309 Mg (340 tons). The time required per cycle is very short — from 45 to 60 minutes.

The BOF has displaced the open hearth as the major steel production process, but is much less flexible because of the inherent limitation of 25 percent to 30 percent scrap in the charge. The amount of BOF capacity in an integrated steel plant is, therefore, closely associated with hot metal availability. Additional flexibility in scrap use can be obtained by preheating the scrap with an oxygen-fuel burner. In many steel plants, the open hearth shop is modernized and equipped with appropriate pollution control equipment so that it can be used in conjunction with BOF shops to provide the required flexibility to accommodate variations in hot metal-scrap ratio. A combination of BOF shops and electric furnace shops provides the maximum in flexibility and may represent the makeup of future steelmaking facilities.

Excluding fuel use for scrap preheating, other uses are for refractory dryout and to keep the BOF vessel from cooling between heats. Their uses amount to about 232 kg per kg (200,000 Btu per ton) of steel produced.

Decarburization of the iron charged to the BOF produces about 467 kJ of carbon monixide per kilogram of steel (400,000 Btu/ton). The off-gases also contain large amounts of particulates, which must be removed before discharge into the atmosphere. Typical American practice is to burn the combustible gases in water-cooled hoods mounted above the BOF vessel, cool with excess air or water sprays, and pass the cooled gases through high-energy scrubbers or electrostatic precipitators. In most cases, the BOF vessels are equipped with open hoods that admit air for combustion of carbon monoxide on a relatively uncontrolled basis. If additional steam can be used in the plant, the combustion hood can be used as a steam generation device, although the steam production will only be cyclic. Some new plants use suppressed combustion hoods which do not inspire air and burn off-gases. New BOF capacity is expected to continue this trend, which may cause a decrease in total NO_x emissions.

During the combustion of the waste gas, the potential for NO_x production exists. One steel manufacturer gives a range of values of from 30 to 80 ppm, or 180 to 500 ng NO_x per kg (0.36 to 1.0 lb NO_x per ton) of steel produced. There is no information available on NO_x control techniques for the basic oxygen furnace (Reference 5-28).

Soaking Pits and Reheat Furnaces

These are large furnaces with fuel inputs ranging from 1.17 to 4.12 MJ/kg (1.0 to 3.5 x 10^6 Btu/ton) heated. Fuel efficiency is affected by many factors such as furnace size, design, combustion controls, combustion air temperature, furnace scheduling, and downtime. Improved efficiency measures, which do not increase flame temperature, will, in general, reduce NO_x emissions in proportion to the reduction in fuel usage.

Existing fuel conservation measures in soaking-pit heating include improved scheduling so as to charge at a higher ingot temperature, programmed input control, improved burner designs, air/fuel ratio control responsive to stack-gas oxygen content, addition of recuperators to existing cold combustion air installations, and use of recuperators designed to give higher preheat temperature. Of these, the use of high-mixing-rate burners and an increase in combustion air preheat are likely to increase the NO_x emission level. At the present time, only experimental information is available concerning the effect of these parameters on NO_x levels.

Soaking-pit and reheat-furnace operating temperatures are such that the estimated NO_x levels should fall in the 250 to 350-ppm range. However, the very large amounts of fuel used result in a total NO_x output estimated at 97 Gg (107,000 tons) in 1971.

A major factor that will reduce consumption of purchased and in-plant fuels and thereby decrease NO_x output is the trend toward use of continuous casting to replace some ingot casting. In this process, billets and slabs which are hot-rolled prior to cooling are produced from molten steel, thus eliminating soaking-pits and most of the reheat requirement. About 20 percent of total steel production, or 36 Tg (40×10^6 tons), is estimated to be produced by continuous casting in 1985. In spite of this, soaking-pit and reheating furnace steel capacity will have to be increased during the 1975 to 1985 period to provide for the expected growth in steel production and for the steel which for process reasons will have to be cast in ingots. According to the IGT projection, conventional steel processing will account for 144 Tg (160×10^6 tons) in 1985. At present fuel consumption of 5.4 MJ/kg (4.7×10^6 Btu/ton), the total fuel consumed for soaking-pits and reheat furnaces in 1985 will be 795 PJ (750×10^{12} Btu). This fuel consumption will result in estimated NO_x emissions of 143 Gg (157,900 tons).

Heat Treating and Finishing Operation

This category includes annealing, hardening, carburizing and normalizing of some of the steel industry cold-rolled products, as well as production of coated products. Fuel consumption in 1971 was about 632 PJ (600×10^{12} Btu) for the production of cold-rolled products (about 25 percent of total steel production). NO_x emission levels are assumed to be in the 150 to 250-ppm range. On this basis, total NO_x emission in 1971 for this category will be about 7.6 Gg (8,400 tons). Assuming that production of cold-rolled products remains at about 25 percent of total steel production, the 1985 NO_x emission will amount to 10 Gg (11,200 tons) per year. There is no information available concerning NO_x control techniques for these sources (Reference 5-28).

Electric Furnaces

Production of steel in electric-arc furnaces has grown rapidly since World War II and is currently estimated to be about 20 percent of total steel production. Because of the phase out of open hearth steelmaking, the increase in BOF steel production, and the associated scrap-use limitation, the amount of steel produced in electric-arc furnaces is expected to increase even more.

The combustion of fossil fuels currently plays a very small role in electric steelmaking. This may change in the future as advances in technology permit the increased use of scrap preheating. Most authorities agree that scrap preheating will be accomplished outside the electric-arc furnace in a specially designed charging bucket, probably equipped for bottom discharge. Many of the designs use excess air burners to limit flame temperature and minimize oxidation of the scrap. Associated air-pollution problems include particulates from dirty scrap, iron oxide, and oil vapors. The requirement for both incineration at or above 1,033K (1,400F) and particulate removal has caused shutdown of several scrap preheating installations because of economic considerations.

The use of electricity for heat in steel production transfers the NO_x emissions to the utility plant where the problem is easier to control. Electric furnaces are, in any case, a very minor source of NO_x from the steel industry (Reference 5-28).

5.3.2.2 Emissions

Emissions in the steel industry and its related processing have historically consisted of fumes, smoke, and dust or particulates. The gases usually considered obnoxious have been SO_2, CO, and odors. The presence of oxides of nitrogen has been obscured by the heavy emission of particulates and a resulting lack of physical evidence. The NO_x emissions observed can be traced largely to the combustion of fuel oils and gas and, in part, to the burning of carbon monoxide, which is a product of the processing operations.

The emission of nitrogen oxides from iron and steelmaking and processing equipment does not appear to have been extensively investigated. However, reasonable estimates can be made by assuming a relationship between known operating temperatures and NO_x concentrations in stack gases (Reference 5-28). This relationship is affected by other variables, such as combustion air preheat temperature and oxygen enrichment of combustion air.

Table 5-7 shows the estimated NO_x concentrations for the major energy-intensive processes and the resulting total annual combustion-related NO_x production based on 1971 steel production energy consumption data (Reference 5-28).

TABLE 5-7. ESTIMATED NO_x EMISSIONS FROM STEEL MILL PROCESSES AND EQUIPMENT (Reference 5-28 except where noted)

Process or Equipment	Annual Fuel Consumption		NO_x Emission Factors[a]			Annual NO_x Emissions[a]	
	PJ	10^{12} Btu	ppm (as measured)	ng/J	lb/10^6 Btu	Gg	tons
Pelletizing	29	27	300	180	0.42	5.1	5670
Sintering	98	93	500 (230)[e]	300	0.70	29.6	32550
Blast Furnace	nd[b]	nd	neg[c]	neg	neg	neg	neg
Coke Oven	225	212	200 (10-485)[e]	120	0.28	26.9	24680
Blast Furnace Stove	212	200	100	60	0.14	12.6	14000
Open Hearth Furnace	135	127	600	360	0.84	48.3	53340
Basic Oxygen Furnace	nd	nd	nd	nd	nd	nd	nd
Soaking Pit and Reheat Furnaces	541	510	300 (92)[e]	180	0.42	96.4	107100
Heat Treating and Finishing	64	60	200	120	0.28	7.6	8400
Electric Furnaces[d]	nd	nd	6-25	nd	nd	.02-.09	26-110

Notes: [a] expressed as NO_2
[b] nd = no data
[c] neg = negligible emissions
[d] Reference 5-37
[e] American Iron and Steel Institute test data provided by Dr. Walter Jackson (U.S. Steel), (Reference 5-36)

Other test results provided by the American Iron and Steel Institute (Reference 5-36) indicate different emission factors as shown in parentheses in Table 5-7. The emission levels for the coke ovens are the result of three separate tests (10, 186, and 485 ppm). There was some concern about the experimental procedures, and new tests are planned for 1978.

Results of recent tests reported by Hunter, et al. (Reference 5-26) are summarized in Table 5-8. The open hearth furnace was tested while operating on natural gas and Number 6 fuel oil (60/40). The wide fluctuations in NO_x and CO observed as various operations were performed are shown in Figure 5-5. Large changes in excess air occurred as the operators opened doors to look at the steel and to add material or adjust fuel flow to change heating rate. NO_x emissions varied from 100 to 3500 ppm and averaged about 1800 ppm or about 950 ng/J (2.2 lb/MMBtu). NO_x increased somewhat linearly with excess O_2. Particulate emissions were 2200 ng/J (5.02 lbMMBtu), measured upstream of the precipitator. Following baseline tests the furnace was overhauled to repair refractory and fix leaks. A second test cycle was observed on the repaired furnace and the average NO_x was 1094 ng/J (1250 ppm), a reduction of about 40 percent. During baseline tests, NO_x frequently exceeded 2000 ppm but with the excess air controlled, excursions over 2000 ppm occurred only twice.

One steel billet reheat furnace was tested while firing natural gas at heat rates between 13 and 30 MW. Baseline NO_x emissions at 24 MW (82 million Btu/hr) were 56 ng/J (110 ppm) and particulates were 17 ng/J (0.04 lb/MMBtu). This furnace had two heating zones with 13 and 14 burners, respectively. The row with 13 burners released about 80 percent of the heat input. Combustion modifications included reduced excess air, resulting in a 24 percent NO_x reduction, and burners out of service which produced a 43 percent NO_x reduction with three burners out of service in the row of 13 burners.

One steel ingot soaking pit was tested (site 16/2) while firing natural gas at about 2.9 MW (10 MMBtu/hr) through a single burner. Baseline NO_x emissions at 2 MW were 52 ng/J (101 ppm). Reduction of excess air reduced NO_x by 69 percent with no adverse effect on the steel.

5.3.3 Glass Manufacture

5.3.3.1 Process Description

The glass manufacturing industry is made up of several basically different types of operations. They are:

TABLE 5-8. EFFECTS OF NO_x CONTROLS ON STEEL INDUSTRY NO_x EMISSIONS (Reference 5-26)

Device Type	Fuel	Average Baseline NO_x		Max. % Reduction	Combustion Modification
		ng/J	ppm @ 3% O_2		
Steel Open Hearth Furnace	Nat. Gas + No. 6 Oil	1094	2070	40	Low O_2
Steel Reheat Furnace	Nat. Gas	56	110	43	3/27 BOOS
Steel Soaking Pit	Nat. Gas	52	101	69	Low O_2

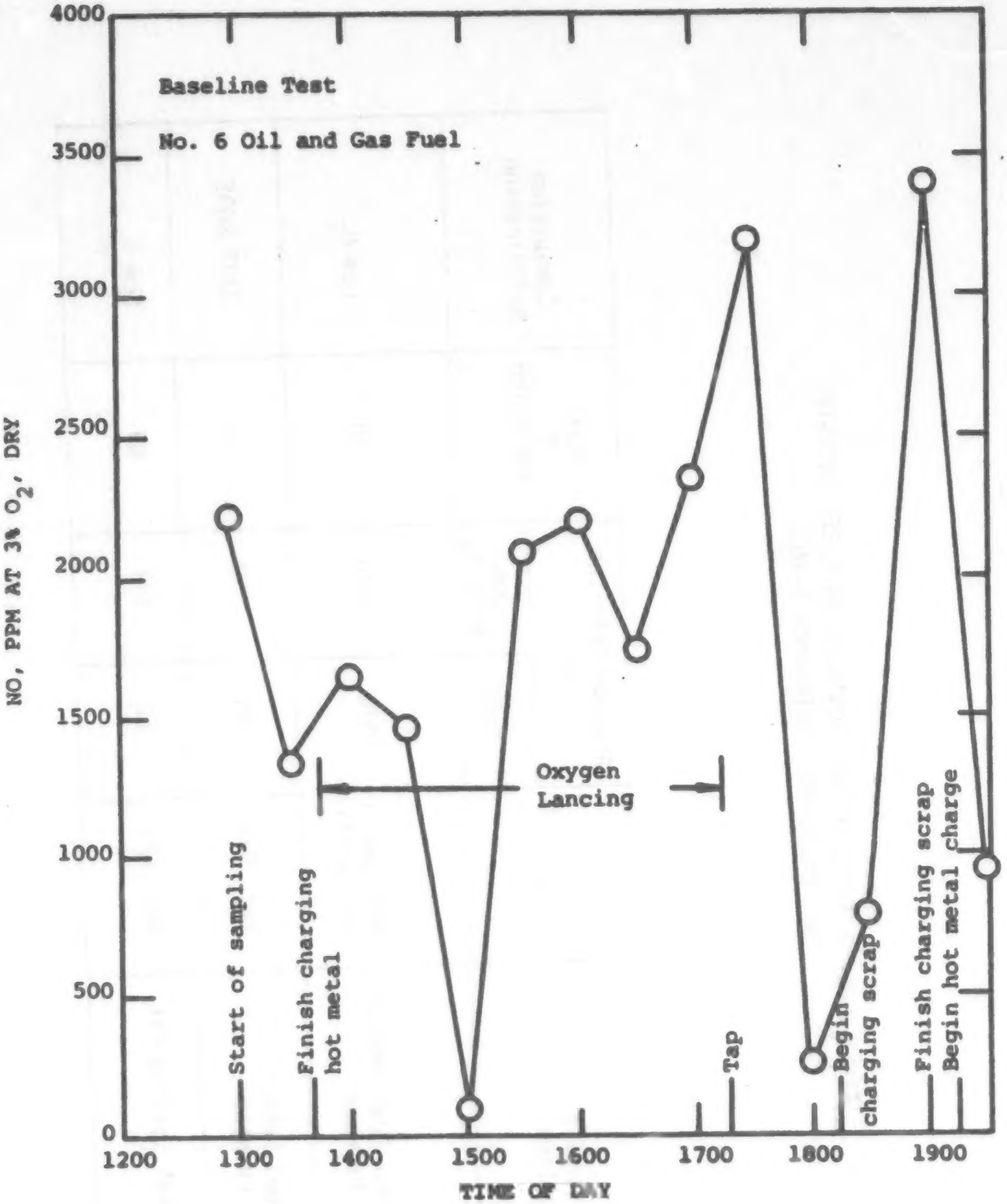

Figure 5-5. NO emissions as a function of time for an open hearth furnace (Reference 5-26).

1. Glass container manufacture
2. Fiberglass manufacture
3. Flat glass manufacture
4. Specialty glass manufacture

The largest type is the glass container industry, which produces about 45 percent of the total amount of glass (by weight) produced by the entire industry.

While the specific processes used within each segment of the industry vary according to the product being manufactured, glass manufacturing involves three major energy-consuming processes: melting the raw materials, refining the molten glass, and finishing the formed products. Typically, about 80 percent of the energy consumed by the glass industry is for melting and refining, 15 percent is for finishing, and 5 percent is for mechanical drives and conveyors. The primary differences in processes used among the various segments occur in the refining and finishing operations.

The raw materials used in glass manufacture consist primarily of silica sand, soda ash, limestone, and cullet (crushed waste glass). In the production of window and plate glass, for example, temperatures in the range of 1,783K to 1,838K (2,750F to 2,850F) may be required to melt these raw materials into a viscous liquid.

The furnaces used are of the pot type if only a few tons of a specialty glass are to be produced, or of the continuous tank type for larger quantities. By far the larger amount of glass is melted in furnaces, and only these will be considered in connection with NO_x control.

Continuous reverberatory furnaces have a holding capacity of up to 1.27 Gg (1,400 tons) and a daily output of as much as 270 Mg (300 tons). Reverberatory furnaces in this industry are broken into two classifications according to the firing arrangement used: end-port and side-port melters. In the operation of a side-port-fired furnace, the preheated combustion air mixes with the fuel in the port, resulting in a flame that burns over the glass surface. The products of combustion exit via the opposite port, down through the checkerbricks, and out through the reversing valve to the exhaust stack. Typically, there are several ports situated along each side of the furnace. In contrast, there are only two ports in an end-port-fired furnace, located on the rear wall of the furnace. The flame is ignited in one port, travels out over the glass toward the bridgewall, and "horseshoes" back to the exit port — the other port in the rear of the furnace. In both types of furnaces, the firing pattern is reversed every 20 to 30 minutes, depending upon the specific furnace. During this reversal period, the flame is extinguished, the furnace is purged of combustion gases by reversing the flow of combustion air and exhaust gases passing through the reversal valve, and combustion is then reestablished in what was previously the exhaust port. Both types of melters are operated continuously throughout a campaign that normally lasts 4 to 5 years, at sustained temperatures up to 1,867K (2,900F).

In addition to the reverberatory-type melters, day tanks, unit melters, and pot melters are used, mostly in the pressed and blown glass industry. Many of these melters are batch-type, as opposed to continuous, resulting in a substantial reduction in fuel-utilization efficiency. Much of the fuel that is wasted is due to the antiquated methods of operation and associated equipment used with these melters (Reference 5-28).

The combustion gases, on leaving the melting zone, retain a considerable amount of heat. This is reclaimed in a regenerator or brickchecker chamber. When the firing cycle is reversed, combustion air is preheated by being passed through the brick work. Preheating saves fuel but increases the flame temperature which promotes NO_x formation.

Coal is not used in glass melting. Since molten glass is conductive, electrical heating is used as a booster to supplement fuel firing whenever technically and economically practical. Gas and, to a lesser extent, fuel oil are the preferred fuels.

5.3.3.2 Emissions

The flue gas from glass-melting furnaces is the major source of NO_x emission in the glass industry. The operation of these furnaces is similar to that of open hearth furnaces used in steelmaking; regenerative checkerwork sets absorb heat from the combustion gases for subsequent release to the incoming combustion air. This is accomplished by a reversing valve which puts each checkerwork set through its heating and cooling cycle in turn. The sequence of intense high-temperature combustion and quenching in the checkerwork sometimes raises NO_x emissions to levels higher than those experienced in a steam boiler of equivalent heat release. For example, during a recently completed experimental program, NO_x emissions were measured during a complete firing cycle of a glass melter. NO_x emissions were highest at the beginning of the firing cycle and then, as the cycle continued, decreased by about 30 percent. At the beginning of the firing cycle, the combustion air is preheated to a higher temperature, which results in a hotter flame than at the end of the cycle when the checkerbrick and hence the air have cooled considerably. Other major factors in NO_x formation in a glass melter, such as flame velocity and recirculation patterns of flue gases, are being studied.

Table 5-9 summarizes the emissions from several glass melters as measured by a number of investigators.

TABLE 5-9. NO_x EMISSIONS FROM GLASS MELTING FURNACES

Investigator	NO_x (ppm as measured)	Comments
IGT (Reference 5-41)	490 to 700	gas fired; 8% excess air
Ryder and McMackin (Reference 5-42)	450 to 600	25% to 45% excess air
Stockham (Reference 5-38)	340	excess air unknown
Mills, et. al., (Reference 5-39)	435 to 1320 (average of 570)	———
Danielson (Reference 5-40)	137 725	amber glass melting flint glass melting

5.3.3.3 Control Techniques

According to representatives of the glass industry, the efforts of the industry to reduce air pollutant emissions are severely hampered by the variations in regulations that exist from state to state. This lack of uniformity requires that different solutions to the problem be sought, depending on the location of the specific plant. This, in turn, adds substantially to the cost of pollution control. In addition, not only are the regulations variable from one location to another, but these regulations are constantly changing. As a result, very few air pollution control equipment installations have been made on glass furnaces, and there is very little data available on the effectiveness and cost of these devices.

In general, SO_x, NO_x, and particulates are the primary air pollutants from the glass manufacturing processes. The concern is primarily with the melting process because this is the largest energy consumer and the major contributor to air pollutant emissions. The major pollution problem in the combustion process is NO_x emissions.

While the formation of NO_x in the combustion process is not entirely understood, it is clear that the goals of reducing NO_x emissions and reducing energy consumption are seemingly at odds. NO_x formation is a temperature-related phenomenon; as temperature increases, NO_x emissions increase. On the other hand, increasing available heat to a process may result in increases in efficiency and in temperature, which in turn increase NO_x emissions. Analysis of the process modifications under consideration in the glass industry shows that there is a possibility of increasing NO_x emissions. If the implementation is carried out properly, however, this need not occur.

Six recommended modification programs are listed in Table 5-10. The order of listing is according to programs that afford the greatest potential for solving the problems in the shortest period of time. The table also presents estimates of improvements that may be obtained, where such estimates can reasonably be made (Reference 5-28). Cost data for these programs are not available at this time. Two of the six recommendations are currently being pursued by EPA/IERL-Cincinnati.

5.3.4 Cement Manufacture

5.3.4.1 Process Description

The cement industry includes all establishments engaged in the manufacture of hydraulic cement (generic name: portland cement), masonry, natural, and pozzuolana cements. This discussion is limited to the production of portland cement because it accounts for 95 percent of the total

TABLE 5-10. RECOMMENDED PROGRAMS FOR REDUCING EMISSIONS AND ENERGY CONSUMPTION IN THE GLASS INDUSTRY (REFERENCE 5-28)

Program	Expected Improvements in Energy Consumption, %	Expected Improvements in Air Pollutant Emissions
1. Develop current emission data	—	—
2. Raw batch pretreatment — i.e., preheating and agglomeration	25-50	25% to 50% potential NO_x reduction, may reduce particulate in form of batch carry-over
3. Oxygen enrichment	5-15	No effect on NO_x, SO_x, or particulates
4. Augmentation of heat transfer from flames — e.g., burner positioning	10-20	Proportional NO_x reduction
5. Use of low-temperature heat for driving compressors	—	—
6. Development of submerged combustion process	50	Will substantially reduce NO_x emissions

cement manufactured in the United States, with the remaining 5 percent split among the other types.

Raw materials used in the manufacture of portland cement consist of limestone, chalk or marl, and seashells. These are combined with either clay, shale, slate, blast furnace slag, iron ore, or silica sand. The end product is a chemical combination of calcium, silicon, aluminum, iron, and other trace materials. The raw materials are first ground and blended together. Depending upon which of the two processes is used, water may be added during blending (the wet process) or the ingredients can be mixed on a dry basis (the dry process). In general, the moisture content of the raw materials determines the process used. If the moisture content is greater than 18 percent, by weight, the wet process will be used. If the moisture content is less than 18 percent, the dry process will be used. The next step is the calcining or burning of the mixed raw material in a rotary kiln. During this step, the material is heated to approximately 1,755K (2,700F) and transformed into clinker, which has different chemical and physical properties than the raw materials had initially. The clinker is discharged from the kiln and cooled. The last step is to grind the clinker to the desired fineness and add gypsum to control the setting time of the concrete (Reference 5-28).

5.3.4.2 Emissions

The major air pollutant emission problem in the manufacture of portland cement is particulates, which occur in all phases of cement manufacturing from crushing and raw material storage to clinker production, clinker grinding, storage, and packaging. However, emissions also include the products of combustion of the fuel used in the rotary kilns and drying operations; these emissions are typically NO_x and small amounts of SO_x. For both the wet and dry kiln processes, the limited data shows that nitrogen oxides are emitted at a rate of about 1.3 g per kg (2.6 lb per ton) of cement produced.

The largest source of emissions in cement plants is the kiln operation. At present, about 56 percent of the cement kilns in operation use the wet process, and 44 percent use the dry process. Based on this information, estimates of total NO_x emissions from cement plants in 1972 are 42.7 Gg (4.7×10^4 tons) for the dry process and 54.5 Gg (6×10^4 tons) for the wet process. These estimates, because of a lack of data, assume the use of no controls by the industry. Without an inventory of control equipment in use, they cannot be refined.

Future efficiency-improving process modifications that increase flame temperature without improving heat transfer to the process load will almost certainly result in increased NO_x emissions.

Conversely, adequate removal of the additional heat resulting from the applicable process modifications should maintain NO_x emissions at their current level.

Of the process modifications deemed to be near-term, only the use of oxygen enrichment has any great potential of increasing air pollutant emissions, primarily NO_x. In some applications in other industries, for example, glass melting, oxygen enrichment can be used without increasing NO_x emissions. However, due to the different type of load in the cement industry and the different patterns of heat transfer, it is suspected that NO_x would increase with the implementation of oxygen enrichment (Reference 5-28).

5.3.4.3 Control Techniques

There is very little information in the literature regarding commercial installation of equipment for removing NO_x from kiln waste gas or of modifications to kiln operations to reduce NO_x production. Water scrubbing is sometimes used for particulate removal from waste gas from lime kilns. In this operation, the gas contacts a slurry of calcium hydroxide, which should remove a 50/50 mixture of NO and NO_2 and reduce NO_x up to 20 percent. Flue gas recirculation, which is used to control temperature in some lime kilns, should reduce NO_x emissions by lowering flame temperature.

Reference 5-26 reports NO_x emission test results for both a dry process kiln and a wet process kiln. The dry process kiln was tested at full capacity while firing a 68/32 mixture of coke and natural gas. Data for the same kiln firing natural gas and oil separately were also available for comparison. Emissions of NO_x while firing natural gas were 1,050 to 1,800 ng/J (1680 to 2900 ppm). Operation on oil resulted in a 60 percent reduction (400-710 ng/J). Operation on combined coke and natural gas produced emissions of 655 to 710 ng/J, a 50 percent reduction.

Lower NO_x emissions on solid and liquid fuels compared to gas are attributed to the highly adiabatic nature of the process. Many cement kilns are currently being converted from gas to solid fuels. This conversion will be beneficial in reducing NO_x and could be pursued as an NO_x control method that is consistent with the reduction of industrial gas consumption.

The wet process cement kiln was tested only while firing natural gas and had baseline emissions of 1319 ng/J (2250 ppm). Combustion modifications investigated included variation of combustion air inlet temperature and excess oxygen. Increase of combustion air temperature from 644K (700F) to 767K (920F) increased NO emissions to 1518 ng/J, and 15 percent increase. Reduction of excess oxygen at baseline air temperature reduced NO_x to 846 ng/J, a 36 percent reduction. The independent reductions of either excess air or air temperature caused unacceptable reduction of kiln temperature that can result in a process upset. The NO emissions were found to be a strong function of kiln temperature, as shown in Figure 5-6. It was found that simultaneous reduction of excess air and increase in air temperature could produce a reduction in NO of about 14 percent while maintaining kiln temperature.

Electric heating eliminates all the pollutants associated with combustion sources, but its use in kiln operation is very limited. Another means of emission control in kiln operation is the choice of kiln type. Some NO_x reduction in limestone calcining is obtained by using a vertical instead of a rotary kiln. The mechanism of operation is such that heat transfer to the load is very high, and peak temperatures are lower than required to obtain the formation of NO_x in large amounts.

5.3.5 Coal Preparation Plants

Coal in its natural state contains impurities such as sulfur, clay, rock, shale, and other inorganic materials, generally called ash. Coal mining adds more impurities. Coal preparation plants serve to remove these impurities. Coal cleaning processes utilized by coal preparation plants may be wet, dry, or a combination of both. Wet processes are a minor source of oxides of nitrogen.

After the coal is wetted by the cleaning process, primary drying is done mechanically by dewatering screens followed by centrifugal driers. When lower surface moisture is desired (3 to 6 percent) with finer coal sizes, secondary drying is required. Such low moisture levels can best be accomplished by thermal drying. It appears that new coal preparation plants that install thermal dryers will use a fluidized-bed type.

In the fluidized bed drier, hot combustion gases from a coal-fired furnace are passed upward through a moving bed of finely-divided wet coal. As the bed fluidizes, the coal is dried as the fine particles come into intimate contact with the hot gases.

The major pollutant evolved from the thermal dryer is particulate. Well-controlled thermal driers emit only minor quantities of NO_x. Concentrations of 40 to 70 ppm (0.16 to 0.28 kg/MJ, or 0.39 to 0.68 $lb/10^6$ Btu) have been measured (Reference 5-43). These emission rates are below the NSPS of 300 ng/J (0.7 $lb/10^6$ Btu) for large steam generators. In any case, no NO_x standards have yet been proposed since the thermal dryer capacities are generally less than the smallest power plants required to control NO_x emissions: 73.2 MW, or 250×10^6 Btu/hr (Reference 5-43).

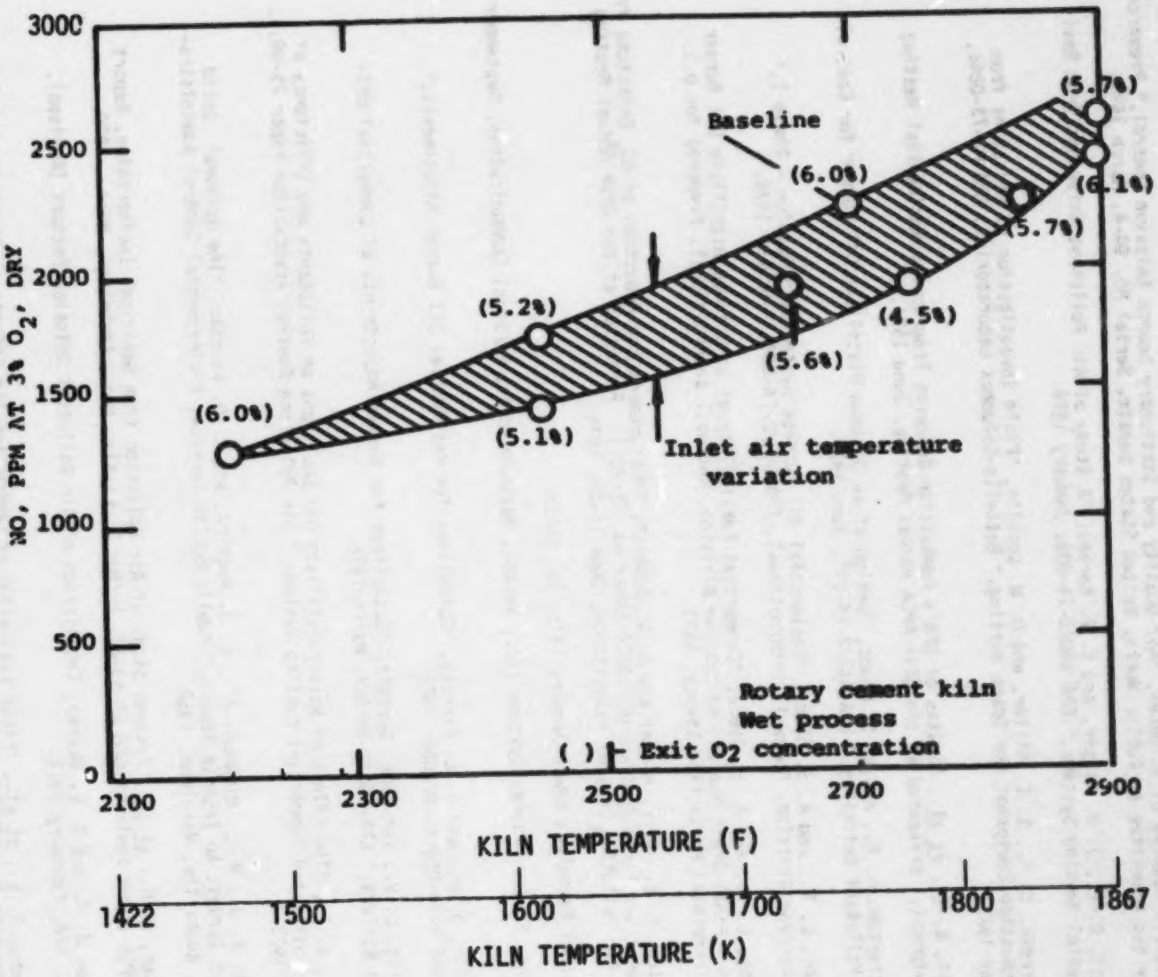

Figure 5-6. The effect of cement kiln temperature on NO emissions (Reference 5-26).

REFERENCES FOR SECTION 5

5-1 National Academy of Sciences, "Air Quality and Stationary Source Emission Control," Prepared for the Committee on Public Works, United States Senate, Serial No. 94-4, March 1975.

5-2 Hall, R. E., J. H. Wasser, and E. E. Berkau, "A Study of Air Pollutant Emissions from Residential Heating Systems," EPA 650/2-74-003, January 1974.

5-3 Barrett, E. R., S. E. Miller, and D. W. Locklin, "Field Investigation of Emissions from Combustion Equipment for Space Heating," Battelle-Columbus Laboratories, EPA R2-73-084a, June 1973.

5-4 Hall, R. E., et al., "Status of EPA's Combustion Research Program for Residential Heating Equipment," presented at the 67th APCA Annual Meeting, June 1974.

5-5 Dickerson, R. A., and A. S. Okuda, "Design of an Optimum Distillate Oil Burner for Control of Pollutant Emissions," EPA-640/2-74-047, June 1974.

5-6 Combs, L. P., and A. S. Okuda, "Residential Oil Furnace System Optimization — Phase I," Rocketdyne Division, Rockwell International, EPA-600/2-76-038, February 1976.

5-7 Combs, L. P., and A. S. Okuda, "Commercial Feasibility of an Optimum Distillate Oil Burner Head," Final Draft Report, Rocketdyne Division, Rockwell International, Prepared for U.S. Environmental Protection Agency, 1975.

5-8 Belles, F. E., R. L. Himmel and D. W. DeWerth, "Measurement and Reduction of NO_x Emissions from Natural Gas Fired Appliances," APCA Paper No. 75-09.1. Presented at the 68th Annual Meeting of the Air Pollution Control Association, June 15-20, 1975.

5-9 National Petroleum News, January 1975, pp. 34-35.

5-10 Lenney, R. J., Blueray Systems Inc., Weston, Massachusetts, Personal Communication, September 1975.

5-11 Locklin, D. W., and R. E. Barrett, "Guidelines for Residential Oil Burner Adjustments," EPA-600/2-75-069-a, October 1975.

5-12 Locklin, D. W., and R. E. Barrett, "Guidelines for Burner Adjustments of Commercial Oil-Fired Boilers," EPA-600/2-76-088, March 1976.

5-13 Hall, R. E., "The Effect of Water/Distillate Oil Emulsions on Pollutants and Efficiency of Residential and Commercial Heating Systems," Air Pollution Control Association Paper 75-09.4, June 1975

5-14 Black, R. J., H. L. Hickman, Jr., A. J. Muchick, and R. D. Vaughan, "The National Solid Wastes Survey: An Interim Report," Public Health Service, Environmental Control Administration, Rockville, Maryland, 1968.

5-15 Niessen, W. R., et al., Systems Study of Air Pollution from Municipal Incineration, Report to NAPCA under contract CPA 22-69-23, Arthur D. Little, Inc., Cambridge, Mass., 1970.

5-16 McGraw, J. J. and R. L. Duprey, Compilation of Air Pollutant Emission Factors (Revised), AP-42, EPA, February 1972.

5-17 Stenburg, R. L., et al., "Field Evaluation of Combustion Air Effects on Atmospheric Emissions from Municipal Incinerators," J. Air Pollution Control Assoc., Vol. 12, pp. 83-89, February 1962.

5-18 Kirsh, J. B., "Sanitary Landfill," In: Elements of Solid Waste Management Training Course Manual Public Health Service, Cincinnati, Ohio, 1968, p. 1-4.

5-19 Fife, J. A., and R. H. Boyer, Jr., "What Price Incineration Air Pollution Control?," Proceedings of 1966 National Incinerator Conference, American Society of Mechanical Engineers, New York. 1966.

5-20 OAQPS Data File of Nationwide Emission, 1971. National Air Data Branch Monitoring and Data Analysis Division, May 1973.

5-21 Chi, C. T., and D. L. Zanders, "Source Assessment: Agricultural Open Burning, State-of-the-Art," EPA-600/2-77-107a, July 1977.

5-22 Air Pollution Problems from Refuse Disposal Operations in the Delaware Valley, Department of Public Health, Air Management Services, Philadelphia, Pa., February 1969.

5-23 Wiley, J. S. *et al*., "Composting Developments in the U.S.," Combust. Sci. 6(2):5-9, 1965.

5-24 Kurkey, C., "Reducing Emissions from Refuse Disposal," J. Air Pollution Control Assoc., 19: 69-72, February 1969.

5-25 Personal Communication, Mr. Peter L. Cook, Office of Federal Activities, U. S. Environmental Protection Agency, November 1977.

5-26 Hunter, S. C., *et al*., "Application of Combustion Modifications to Industrial Combustion Equipment, "*Proceedings of the Second Stationary Source Combustion Symposium, Vol. III*, EPA-600/7-77-0736, July 1977.

5-27 Bartz, D. R., *et al*., "Control of Oxides of Nitrogen from Stationary Sources in the South Coast Air Basin of California," PB 237 688/7WP, September, 1974.

5-28 Ketels, P. A., J. D. Nesbitt, and R. D. Oberle, "A Survey of Emissions Control and Combustion Equipment Data in Industrial Process Heating," Final Report by Institute of Gas Technology for EPA, IGT Project No. 8949, June 1976.

5-29 Schultz, E. J., L. J. Hellenbrand, and R. B. Engdahl, "Source Sampling of Fluid Catalytic Cracking Plant of Standard Oil of California, Richmond, California," Battelle-Columbus Labs, July 1972.

5-30 Schultz, E. J., L. J. Hellenbrand, and R. B. Engdahl, "Source Sampling of Fluid Catalytic Cracking, CO Boiler and Electrostatic Precipitators at the Atlantic Richfield Company, Houston, Texas," Battelle-Columbus Labs, July 1972.

5-31 Shea, E. P., "Source Testing, Standard Oil Company, Richmond, California," Midwest Research Institute, Kansas City, Missouri, 1972.

5-32 Cowherd, C., "Source Testing, Standard Oil of California Company, El Segundo, California," Midwest Research Institute, Kansas City, Missouri, 1972.

5-33 Shea, E. P., "Source Testing, Atlantic Richfield Company, Wilmington, California," Midwest Research Institute, Kansas City, Missouri, January 1972.

5-34 McGannon, H. E., *The Making, Shaping and Treating of Steel*, 8th ed., Pittsburgh, United States Steel Co., 1964.

5-35 Russel, C. C., "Carbonization." In: *Kirk-Othmer Encyclopedia of Chemical Technology*, Standen, A. (ed.), Vol. 4, 2d ed., New York, Interscience Publishers, Inc., 1964, p. 400-423.

5-36 Personal communication, Dr. Walter Jackson, u. S. Steel, November, 1977.

5-37 Personal Communication, Mr. Andrew Trenholm of the Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Durham, North Carolina, May 1976.

5-38 Stockham, J. D., "The Composition of Glass Furnace Emission," presented at the 63rd Annual meeting of the Air Pollution Control Association, St. Louis, June 1970.

5-39 Mills, J. L., *et al*., "Emissions of Oxides of Nitrogen from Stationary Sources in Los Angeles County; Oxides of Nitrogen Emitted by Medium and Large Sources," Joint District, Federal, State, and Industry Project, Los Angeles County Air Pollution Control District, Los Angeles, Calif., Report Number 3, April 1962.

5-40 *Air Pollution Engineering Manual*, Danielson, J. A. (ed.). National Center for Air Pollution Control, Cincinnati, Ohio, PHS Publication Number 999-AP-40.

5-41 Nesbitt, J. D., D. H. Larson, and M. Fejer, "Improving Natural Gas Utilization in a Continuous End Port Glass-Melting Furnace," In: Proceedings of the Second Conference on Natural Gas Research and Technology, Session IV, Paper 9, Chicago, 1972.

5-42 Ryder, R. J., and J. J. McMackin, "Some Factors Affecting Stack Emissions from a Glass Container Furnace," Glass Ind., 50, June-July, 1969.

5-43 "Background Information for Standards of Performance: Coal Preparation Plants; Volume 1: Proposed Standards," EPA 450/2-74-021a, October 1974.

SECTION 6

NONCOMBUSTION PROCESSES

The problem of NO_x emissions has been researched in the chemical industry more intensively than anywhere else because it may represent the loss of a valuable raw material. The following sections of this report discuss commercial processes developed for NO_x control in the manufacture and uses of nitric acid.

The NO_x released in vent gases from the manufacture and industrial uses of nitric acid, differs markedly from that emitted from a combustion flue gas in concentration, total amount, and the ratio of NO_2 and NO present. The NO_x-containing chemical gas is commonly a process stream which must be recycled with maximum NO_x recovery in order to have an economical process. Vent gas is released only because it is too impure to recycle or too low in concentration for economic recovery. The economic limit with a pure gas, as in nitric acid manufacture, is about 0.1 to 0.3 percent NO_x, or 1,000 to 3,000 ppm. The limit is higher in organic nitrations, such as the manufacture of nitroglycerine, where NO_x content of the vent gas may approach 1 percent NO_x, or 10,000 ppm.

The total amount of NO_x emitted from all chemical manufacturing is about 1.7 percent (203 Gg or 2.2×10^5 tons/yr) of all NO_x from manmade sources in the United States. These processes present problems only in special local areas. The problems have been most serious in military ordance works, which manufacture large volumes of nitric acid and use it in organic nitrations. A single plant like the Volunteer Ordance Works has produced, for example, emissions of NO_x equal to all nonmilitary uses of nitric acid in the United States.

A high ratio of NO_2/NO at high concentrations causes the gases to be visible as a brownish plume. The visibility limit depends on the total amount of NO_2 present in the gas volume or layer observed. A convenient rule of thumb is that a stack plume or air layer will have a visible brown color when the NO_2 concentration exceeds 6,100 ppm divided by the stack diameter in centimeters (Reference 6-1). This means that the threshold of visibility for a 5 cm-diameter stack is about 1,200 ppm of NO_2 and for a 30 cm-diameter stack, 200 ppm of NO_2 (or 2,000 ppm of NO_x at a 1:10 ratio of NO_2:NO).

The distinction between NO_2 concentrations and total amount can be quite important in chemical vent gases, since a short burst of NO_2 at 10,000 ppm may be visible but less hazardous than many times as much NO_x emitted from a large stack at a lower concentration. The total amount in a short, concentrated emission may be too small to have a detectable effect on NO_x levels in ambient air.

A large amount of research with varying degrees of success has been carried out on the development of processes for the removal of NO_x from the off-gas resulting from the manufacture and uses of nitric acid. The abatement processes are discussed in detail in Section 6.1.3.

6.1 NITRIC ACID MANUFACTURE

Nitric acid plants are divided into two types: those that make dilute nitric acid (50-68 percent nitric acid) and those that make strong nitric acid (over 95 percent nitric). Nitric acid and water form an azeotropic (constant-boiling) mixture at about 58 percent nitric acid content; this is the limiting factor in the nitric acid concentration available through distillation and absorption methods. The acid is concentrated to 98 percent in an acid concentration unit using extractive distillation. The direct process for making strong nitric acid usually depends on direct formation of nitric acid in an autoclave where nitrogen oxides react with oxygen and water to form nitric acid. Most (> 95 percent) nitric acid plants presently in operation are of the first kind.

6.1.1 Dilute Nitric Acid Manufacturing Processes

Nitric acid in the United States is made by the catalytic oxidation of ammonia. Air and ammonia are preheated, mixed, and passed over a catalyst, usually a platinum-rhodium complex. The following exothermic reaction occurs:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (\Delta H = -906 \text{ J/mole}) \qquad (6\text{-}1)$$

The stream is cooled to 311K (100F) or less, and the NO then reacts with oxygen to form nitrogen dioxide and its liquid dimer, nitrogen tetroxide.

$$2NO + O2 \rightarrow 2\,NO_2 \rightleftarrows N_2O_4 \qquad (\Delta H = -113 \text{ J/mole}) \qquad (6\text{-}2)$$

The liquid and gas then enter an absorption tower. Air is directed to the bottom of the tower and water to the top. The NO_2 (or N_2O_4) reacts with water to form nitric acid and NO, as follows:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \quad (\Delta H = -135 \text{ J/mole}) \qquad (6\text{-}3)$$

The formation of 1 mole of NO for each 2 moles of HNO_3 makes it necessary to reoxidize NO after each absorption stage since the gas rises up the absorber and limits the level of recovery that can be economically achieved.

Acid product is withdrawn from the bottom of the tower in concentrations of 55 to 65 percent. The air entering the bottom of the tower serves to strip NO_2 from the product and to supply oxygen for reoxidizing the NO formed in making nitric acid (Equation 6-3).

The oxidation and absorption operations can be carried out at low pressure (~ 100 kPa, 1 atm), at medium pressure (400 to 800 kPa or 58 to 116 psia) or at high pressure (1000 to 1200 kPa or 145 to 174 psia). Both operations may be at the same pressure or at different pressures.

Before corrosion-resistant materials were developed, the ammonia oxidation and absorption operations were carried out at essentially atmospheric pressure. This also had advantages compared to the higher pressure processes of longer catalyst life (about 6 months), and increased efficiency of ammonia combustion. However, because of the low absorption and NO oxidation rates, much more absorption volume is required, and several large towers are placed in series. Some of these low pressure units are still in operation, but they represent less than 5 percent of the current U.S. nitric acid capacity.

Combination pressure plants carry out the ammonia oxidation process at low or medium pressure and the absorption step at medium or high pressure. The higher combustion temperature and gas velocity at an increased pressure for the oxidation reaction shortens catalyst's lifetime (1 to 2 months) through increased erosion and lowers the ammonia oxidation conversion efficiency (Reference 6-2). Thus lower pressures in the oxidation process are preferred. On the other hand, higher pressures in the absorption tower increase the absorption efficiency and reduce NO_x levels in the tail gas. Of course these advantages must be weighed against the cost of pressure vessels and compressors.

The choice of which combination of pressures to use is very site specific and is governed by the economic trade-offs between the costs of raw materials, energy and equipment, and process efficiency; and local emissions limits. In the 1960's, combination low pressure oxidation/medium pressure absorption and single pressure (400 to 800 kPa) plants were preferred. Since the early 1970's, the trend has been toward medium pressure oxidation/high pressure absorption plants in Europe and single pressure plants (400 to 800 kPa) in the United States.

6.1.1.1 Single Pressure Processes

In the single pressure process, both the oxidation and absorption processes are carried out at the same pressure — either low pressure (100 kPa or ≃ 1 atm.) or medium pressure (400 to 800 kPa). Single pressure plants are the most common type. Figure 6-1 is a simplified flow diagram of a single pressure process (Reference 6-3). A medium pressure process will be described below.

Air is compressed, filtered, and preheated to about 573K by passing through a heat exchanger. The air is then mixed with anhydrous ammonia, previously vaporized in a continuous-stream evaporator. The resulting mixture, containing about 10 percent ammonia by volume, is passed through the reactor, which contains a platinum-rhodium (2 to 10 percent rhodium) wire-gauze catalyst (for example, 80-mesh and 75-μm diameter wire, packed in layers of 10 to 30 sheets so that the gas travels downward through the gauze sheets). Catalyst operating temperature is about 1,023K. Contact time with the catalyst is about 3×10^{-4} sec.

The hot nitrogen oxides and excess air mixture (about 10 percent nitrogen oxides) from the reactor are partially cooled in a heat exchanger and further cooled in a water cooler. The cooled gas is introduced into a stainless-steel absorption tower with additional air for the further oxidation of nitrous oxide to nitrogen dioxide. Small quantitites of water are added to hydrate the nitrogen dioxide and also to scrub the gases. The overhead gas from the tower is reheated by feed/effluent heat exchangers and then expanded through a power recovery turbine/compressor used to supply the reaction air. The tail gas is then treated by the tail-gas treater for NO_x abatement. The bottom of the tower yields nitric acid of 55 to 65 percent strength.

6.1.1.2 Dual Pressure Processes

In order to obtain the benefits of increased absorption and reduced NO_x emissions from high-pressure absorption, dual-pressure plants are installed. Recent trends favor moderate-pressure oxidation and high-pressure absorption.

A process flow diagram for a dual-pressure plant by Uhde is shown in Figure 6-2. Liquid ammonia is vaporized by steam, heated and filtered before being mixed with air from the air/nitrous oxide compressor at from 300-500 kPa (44 to 72 psia). The ammonia/air mixture is catalytically burned in the reactor with heat recovery by an integral waste heat boiler to generate steam for use in the turbine driven compressor. The combustion gases are further cooled by tail gas heat exchange and water cooling before compression to the absorber pressure of 800-1400 kPa (116 to 203 psia). The

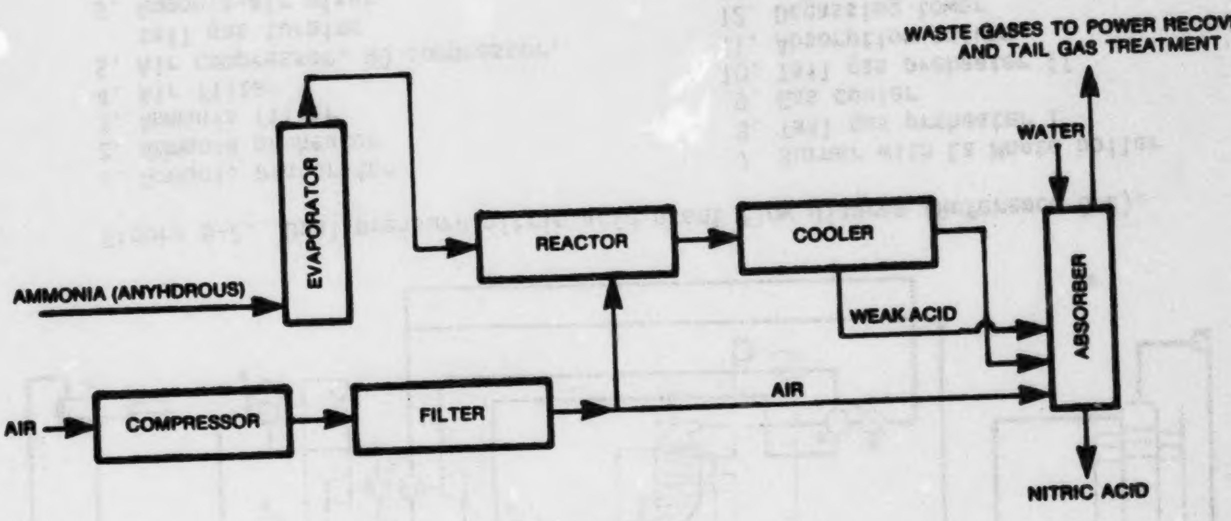
WASTE GASES TO POWER RECOVERY AND TAIL GAS TREATMENT
WATER
AMMONIA (ANHYDROUS)
EVAPORATOR
REACTOR
COOLER
WEAK ACID
ABSORBER
AIR
COMPRESSOR
FILTER
AIR
NITRIC ACID

Figure 6-1. Single pressure nitric acid manufacturing process (Reference 6-3).

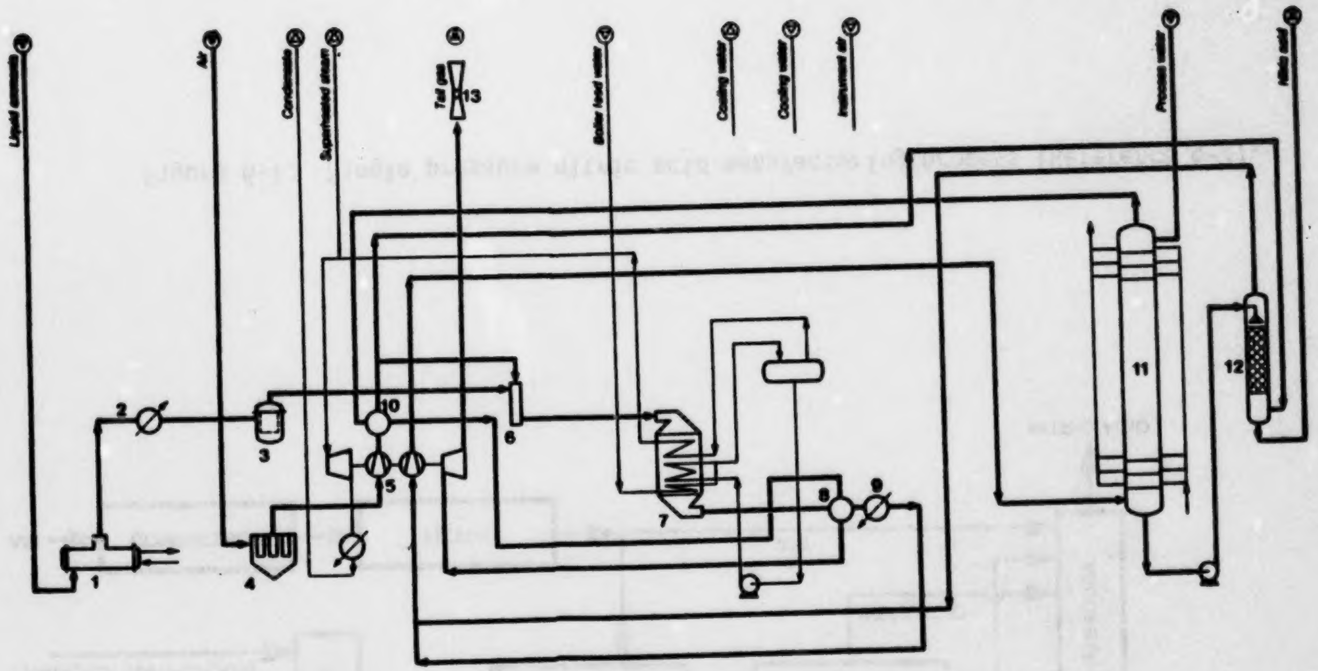
Liquid ammonia
Air
Condensate
Superheated steam
Tail gas
13
Boiler feed water
Cooling water
Cooling water
Instrument air
Process water
Nitric acid
1
2
3
4
5
6
7
8
9
10
11
12

Figure 6-2. Dual pressure nitric acid plant flow diagram (Reference 6-2).

1. Ammonia evaporator
2. Ammonia preheater
3. Ammonia filter
4. Air filter
5. Air compressor, NO compressor, tail gas turbine
6. Ammonia-air mixer
7. Burner with La Monte boiler
8. Tail gas preheater I
9. Gas cooler
10. Tail gas preheater II
11. Absorption column
12. Degassing tower
13. Mixing jet

absorption tower is internally water cooled to increase absorption by water. Nitric acid up to 70 percent concentration is withdrawn from the bottom of the column and degassed with the air feed to remove unconverted NO before being sent to storage. The air/NO mixture is combined with reactor effluent to form the absorber feed. High yields of up to 96 percent conversion and tail-gas emissions as low as 200 ppm NO_2 can be obtained by this process.

6.1.1.3 Nitric Acid Concentration

Figure 6-3 illustrates a nitric acid concentration unit using extractive distillation with sulfuric acid. A mixture of strong sulfuric acid and 55 to 65 percent nitric acid is introduced at the top of a packed column, and flows down the column counter-current to the ascending vapors. Nitric acid leaves the top as a 98 percent nitric acid vapor containing small amounts of NO_x and oxygen, which result from the dissociation of nitric acid. The vapors pass to a bleacher and a condenser to condense nitric acid and separate NO_x and oxygen, which pass to an absorber column for conversion to, and recovery of, nitric acid. Air is admitted to the bottom of the absorber. Dilute sulfuric acid is withdrawn from the bottom of the dehydrating tower and is sent to be concentrated further to be used for other purposes. The system usually operates at essentially atmospheric pressure.

6.1.1.4 Direct Strong Nitric Acid Processes

Nitric acid of high strength can be made directly from ammonia in direct strong nitric acid processes. These processes depend upon the formation of nitric acid by reaction of NO_2 or N_2O_4 with oxygen and water forming 95 percent to 99 percent nitric acid. In this direct process, the composition of the product nitric acid is not restricted by the azeotropic limit.

The principal licensors of these direct processes are Uhde and Davy Powergas. Uhde has built two plants in this country using their direct strong nitric acid process. The Uhde process will be described in detail below. Davy Powergas has two direct strong nitric acid processes; the CONIA process and the SABAR process. Davy has not built any plants utilizing these processes in the United States, but there is a CONIA plant recently constructed in Sweden and a SABAR plant recently constructed in Spain. How these processes differ from the Uhde process will also be described below.

Figure 6-4 shows a process flow diagram for a direct strong nitric acid plant. Air and gaseous ammonia are mixed and reacted where steam is generated in a combination burner/waste heat boiler by the heat of reaction. The reaction products are cooled, and a weak nitric acid condensate removed. The remaining gases are put through two oxidation columns where the NO is converted to NO_2.

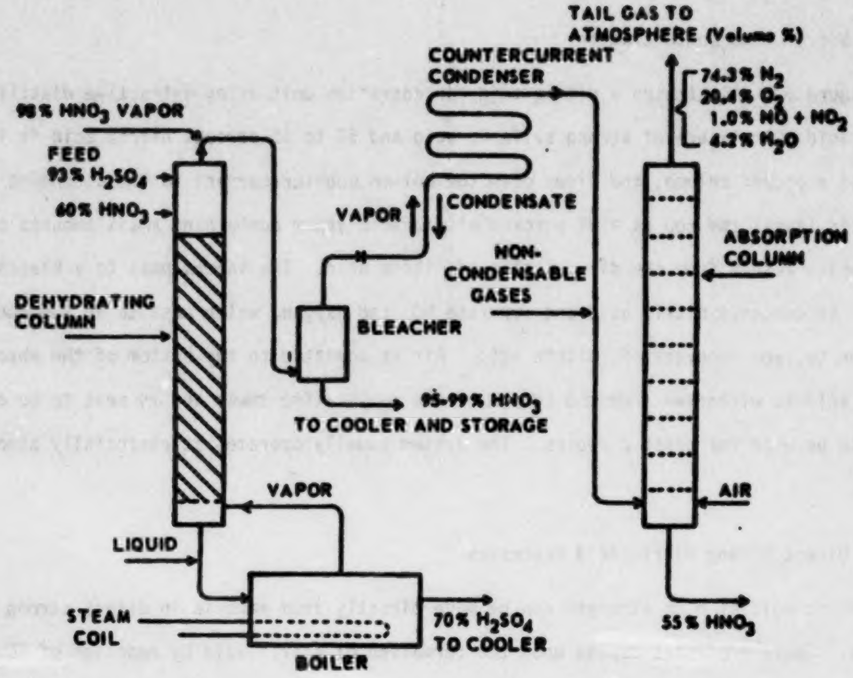
TAIL GAS TO ATMOSPHERE (Volume %)
74.3% N_2
20.4% O_2
1.0% NO + NO_2
4.2% H_2O
COUNTERCURRENT CONDENSER
98% HNO_3 VAPOR
FEED
93% H_2SO_4
60% HNO_3
VAPOR
CONDENSATE
NON-CONDENSABLE GASES
ABSORPTION COLUMN
DEHYDRATING COLUMN
BLEACHER
95-99% HNO_3 TO COOLER AND STORAGE
VAPOR
AIR
LIQUID
STEAM COIL
70% H_2SO_4 TO COOLER
BOILER
55% HNO_3

Figure 6-3. Nitric acid concentrating unit.

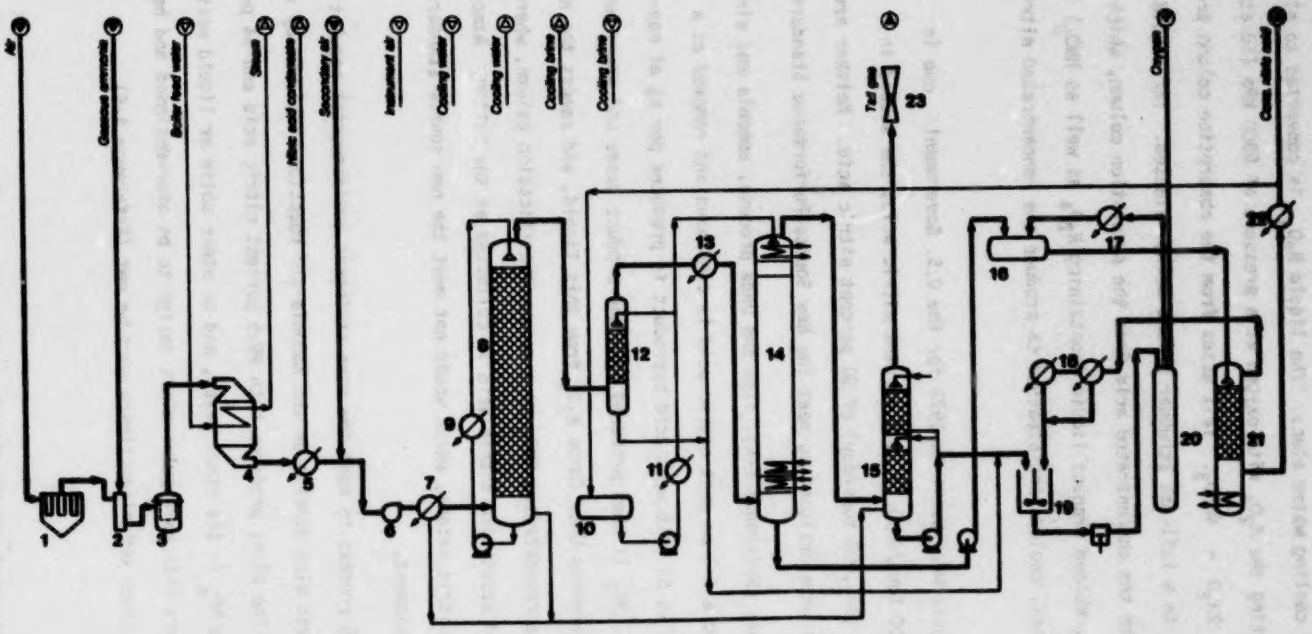
Air
Gaseous ammonia
Boiler feed water
Steam
Nitric acid condensate
Secondary air
Instrument air
Cooling water
Cooling water
Cooling brine
Cooling brine
Tail gas
Oxygen
Conc. nitric acid
1
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Figure 6-4. Process Flow diagram for direct production of highly concentrated nitric acid (Reference 6-2).

1. Air filter
2. Ammonia-air mixer
3. Ammonia gas filter
4. Burner with waste-heat boiler
5. Gas cooler I
6. Blower
7. Gas cooler II
8. Oxidation column
9. Acid cooler
10. Circulating acid tank
11. Acid cooler
12. Final oxidator
13. Brine gas cooler
14. Absorption column
16. Tail gas scrubber
17. Head tank for raw acid
17. Raw acid cooler
18. Liquefier
19. Agitator vessel for raw mixture
20. Reactor vessel
21. Bleaching column
22. Final acid cooler
23. Mixing jet

The overhead vapors are compressed to a pressure that allows the equilibrium di-nitrogen tetroxide (N_2O_4) to be liquefied with the use of cooling water alone. The liquid N_2O_4 is converted to nitric acid of about 95 to 99 percent by reacting the N_2O_4 with oxygen at a pressure of 5000 kPa (50 atm). The conversion reaction is: $2N_2O_4 + 2H_2O \rightarrow 4HNO_3$. Tail gases from the absorption column are scrubbed with water and condensed N_2O_4 in a tail-gas scrubber before being released. The liquid from the tail-gas scrubber is mixed with the concentrated acid from the absorption column, which has been bleached and liquefied. The combined product liquid (containing N_2O_4 as well as HNO_3) is reacted with oxygen in the reactor vessel, cooled, and bleached to produce the concentrated nitric acid.

Both Uhde plants using this process were built in 1973 for the U.S. Government: one in Joliet, Illinois makes 236 Gg/d (260,000 tons/day) of 98.5 percent nitric acid; the second in Chattanooga, Tennessee, makes 313 Gg/d (345,000 tons/day) of 98 percent nitric acid. Neither are in operation at present, although, both were designed to meet the New Source Performance Standards.

In the Davy Powergas SABAR process (Reference 6-4), like the Uhde process, ammonia and air are reacted at atmospheric pressure, and a 2-3 percent nitric acid is condensed and removed as a byproduct. Davy Powergas estimates 0.3 kg of this weak acid byproduct is produced per kg of concentrated acid. As in the Uhde process, NO_2 is then produced from the product gases and absorbed in concentrated nitric acid. However, whereas Uhde forms N_2O_4 from this liquid, and reacts the N_2O_4 with oxygen, the SABAR process takes the concentrated HNO_3 to a vacuum rectification column, where concentrated HNO_3 comes off overhead and azeotropic nitric acid is collected at the bottom. Atmospheric emissions are less than 500 ppm nitric oxides, which would not meet the new source standards in the United States without further treatment.

Davy Powergas developed the CONIA process to meet the more stringent environmental regulations for its site in Sweden. The CONIA process also depends on the ammonia-air reaction, followed by removal of the water which is generated. The plant produces both 99.5 percent nitric acid and 54 percent nitric acid, with less than 200 ppm NO_x in the stack gases, and no other solid or liquid waste streams. However, Davy Powergas considers this particular plant design to be over-designed and hence too costly for most applications unless lower emissions limits must be met (Reference 6-5).

6.1.2 Emissions

Absorber tail gas is the principal source of NO_x emissions from nitric acid manufacturing. Minor sources include nitric acid concentrators and the filling of storage tanks and shipping containers. Nitrogen oxide emissions from nitric acid manufacturing are estimated at 127 Gg

(140,000 tons) during 1974, which is about 1.0 percent of the NO_x emissions from stationary sources. It is estimated that 7.4 Tg (8.2 million tons) of nitric acid (100 percent) were produced in 1974 (Reference 6-6). AP-42 (Reference 6-7) cites an average emission factor for uncontrolled plants of 25 to 27.5 kg/Mg of acid. Typical uncontrolled tail-gas concentrations are on the order of 3000 ppm of NO_x with equal amounts of NO and NO_2 (Reference 6-8). Unde cites emission levels in excess of 800 ppm for low-pressure plants, 400 to 800 ppm for medium-pressure plants, and less than 200 ppm for high-pressure plants (Reference 6-2). The extent of control for these plants is not known, although, Uhde did state that all three processes could be designed in such a way as to meet State and Federal emission limits.

In any nitric acid plant, the NO_x content of tail gas is affected by several variables. Abnormally high levels may be caused by insufficient air supply, high temperature in the absorber tower, low-pressure, production of acid at strengths above design, and internal leaks, allowing gases with high nitrogen oxide content to enter the tail-gas streams. Careful control and good maintenance are required to hold tail-gas nitrogen oxide content to a minimum.

6.1.3 Control Techniques for NO_x Emissions from Nitric Acid Plants

Nitric acid plants can be designed for low NO_x emission levels without any add-on processes. Such plants are usually designed for high absorber efficiency; high inlet gas pressures and effective absorber cooling can lead to low NO_x emissions. However, many new plants, and all existing plants, are not designed for NO_x emission levels low enough to meet present standards. For these plants, add-on abatement methods are necessary.

The available abatement methods suitable for retrofit include chilled absorption, extended absorption, wet chemical scrubbing, catalytic reduction, and molecular sieve adsorption. In this section, these various control techniques for NO_x are described. These techniques may also be appropriate for retrofit of explosive and adipic acid plants.

Many of the retrofit processes are offered by more than one licensor, and many licensors (such as Uhde) offer more than one process. Table 6-1 lists the major processes, the types of plants for which the processes are most suitable, and examples of nitric acid plants where the processes have been applied. (The examples of nitric acid plants are not meant to be inclusive.)

The selection of a control method depends on such things as the degree of control required, the operating pressure of the plant, and the cost and availability of fuel. For example catalytic reduction was used to establish the NSPS originally. Since that time fuel costs have risen to the point where catalytic abatement is not economically attractive for new nitric acid plants but can be used as an effective secondary treatment to meet the NSPS.

TABLE 6-1. NO_x ABATEMENT METHODS ON NEW OR EXISTING NITRIC ACID PLANTS

Process	Method	Comments	Licensors	Examples
Chilled Absorption	Increased solubility of NO_x in chilled water	Usually cannot meet NSPS without other add-on technology or lowered acid product concentration	COL-VITOK	2-318 Mg/d (350 tons/day) (with Gulf catalytic reduction add-on). Nitram, Tampa, Fla.
			TVA	2-50 Mg/d (55 tons/day) plants at Muscle Shoals, (1972)
Extended Absorption	Increased absorption of NO_x by additional absorption equipment	Inlet pressure of 760 kPa required (additional compressors may be required)	J. F. Pritchard (Grande Paroisse)	327 Mg/d (360 tons/day) plant, Miss. Chemicals, Yazoo City, Miss. 1973. 272 Mg/d (300 tons/day) Holston Army Ammunition Plant, Kingsport, Tenn. Cominco Plant, Beatrice Neb. Kaiser, Tampa, Fla. and Bainbridge, Ohio
			P. M. Weatherly	9 U.S. plants, 1 Japan plant (employs chilled absorption process)
			Chemico	908 Mg/d (1000 tons/day) Monsanto, Pensacola, Fla. 1977.
		Requires additional compressor	Uhde	250 Mg/d (275 tons/day) plant, Allied Chemical, Omah, Neb. 1975
			C&I Girdler CoFAZ	None built to date
Wet Chemical Scrubbing	Scrubbing tail gases with urea solution or ammonia to recover NO_x	Performs better at high pressure but operable at lower pressures. Recovers ammonium nitrate and urea solution. Requires refrigeration.	MASAR (urea scrubbing)	Ill. Nitrogen Plt., Marsalles, Ill. Air Products & Chem., Pace, Fla.
			Norsk Hydro (urea scrubbing)	Norsk Hydro, Proggunn, Norway
		May require an evaporator to produce a concentrated ammonium nitrate by product. No refrigeration required.	Goodpasture (ammonia scrubbing)	90 Mg/d (100 tons/day) Goodpasture plt., 1974. Dimmitt, Texas Chevron Oil Co., Richmond, Calif. 1976 C.F. Industries, Fremont, N.D. 2 scrubbers for 7 plants totalling 544 mg/d (600 tons/day). Cyanamid, Welland, Ont.

TABLE 6-1. NO_x ABATEMENT METHODS ON NEW OR EXISTING NITRIC ACID PLANTS (Concluded)

Process	Method	Comments	Licensors	Examples
Catalytic Nonselective	Burns NO_x and O_2 with CH_4 or H_2 to form N_2, H_2O, CO_2	• Consumes natural gas, uneconomical if high NO_x or O_2 content (also reacts with O_2) • May be used in conjunction with extended absorption • Energy recovery possible • Works at low or high pressure	C&I Girdler	Olin, Lake Charles, La. (also, Weatherby plants)
			D. M. Weatherly	IMC Corp., Strelington, La. (1976) (with extended absorption). 817 Mg/d (900 tons/day), 1977. Columbia Nitrogen, Augusta, Ga.
			Chemico	Location not available
Catalytic Selective	Burns NO_x with ammonia to form N_2 and H_2O; O_2 not affected	• Uses ammonia, can be expensive to operate • Often used with extended absorption • Works at low or high pressure • Energy recovery usually not possible • Can achieve very low emission if desired	Gulf	Nitram plants in Tampa, Fla., installed after CDL/VITOK process. 10 plants in U.S.
			Uhde (BASF catalysts)	Plants in Europe and Japan
			Mitsubishi	
Heterogeneous Catalysis	Oxidation of NO + NO_2 catalyzed by heterogeneous catalysis before absorption	Limited success	CDL/VITOK	Under development
Chemical Absorption	Oxidation with $KMnO_4$ ($KMnO_4$ electrolytically reclaimed	Uneconomical not presently offered	Carus Chemical	2 plants in Japan, not currently offered in U.S.
Molecular Sieve	Absorption by molecular sieve, regeneration of the sieve by thermal cycling	• High energy and capital demands • Hard to fit cycling of sieve into continuous plant operation	Purasiv N (Union Carbide)	50 mg/d (55 tons/day) Hercules, Inc. Bersemer, Ala. 1974 50 mg/d (55 tons/day) U.S. Army, Holston, Kingston, Tenn. (inoperable, dismantled)

The inlet pressure at the absorber is an important factor in the selection of NO_x control equipment. In general, extended absorption equipment cannot be economically installed where the equipment will have inlet pressures of less than 758 kPa (110 psia). Consequently, extended adsorption is not usually chosen for older, low pressure nitric acid plants. Wet scrubbing and molecular sieve absorption are also not as effecive at low pressures. Catalytic reduction, however, does not require high pressures.

6.1.3.1 Chilled Absorption

This method is used primarily for retrofit of existing plants. Chilling the water used in a nitric acid absorption tower leads to higher yields of nitric acid and lower NO_x concentrations in the tail gas. Both water and brine solutions have been used in a closed loop system to provide local cooling to the liquid on the trays of the absorption tower. Absorption may be further enhanced by heterogeneous catalytic oxidation of NO to NO_2 upstream of the absorption tower.

CDL/VITOK Process

Figure 6-5 shows a CDL/VITOK process flow diagram. Tail gas enters the absorber, where the gases are contacted with a nitric acid solution to both chemically oxidize and physically absorb nitrous oxides. The reaction of NO to NO_2 may be catalyzed in the main absorber. The upper portion of the absorber is water cooled to improve absorption. The nitric acid solution from the absorber is sent to a bleacher where air removes entrained gases and further oxidation occurs. The bleached nitric acid solution is then either sent to storage or recirculated to the absorber after the addition of make-up water. The process employes a closed loop system to chill the recirculated acid solution and tower cooling water by ammonia evaporation.

One variation in this system proposed by CDL/VITOK includes the addition of an auxilliary bleacher operating in parallel with the primary unit. Another variation uses a secondary absorber with its own bleacher.

At the Nitram, Tampa, Florida location two 318 Mg/d plants were fitted with the CDL/VITOK process. NO_x tail gas concentrations were reduced from 1500 to 1800 ppm to 600 to 800 ppm. With the addition of a gulf catalytic abatement system the plant meets local regulations. A second plant at Nitram fitted with the process showed promise but was shut down and replaced with a new nitric acid plant.

TVA Process

The Tennessee Valley Authority, at their nitric acid plant in Muscle Shoals, Alabama, designed and installed refrigeration for NO_x abatement pruposes in 1972, in order to meet State standards of 2.75

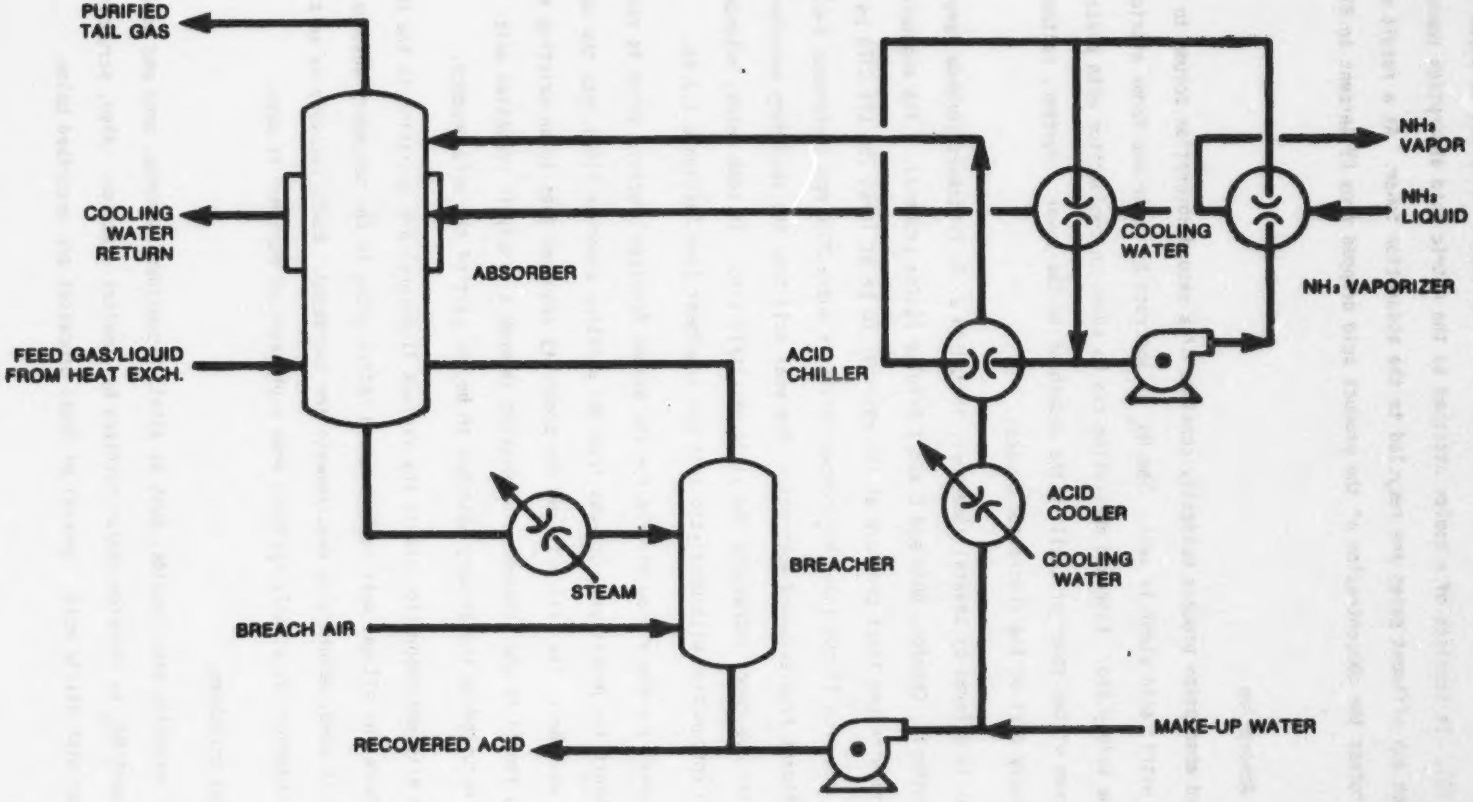
PURIFIED TAIL GAS
COOLING WATER RETURN
ABSORBER
FEED GAS/LIQUID FROM HEAT EXCH.
STEAM
BREACH AIR
BREACHER
RECOVERED ACID
ACID CHILLER
ACID COOLER
COOLING WATER
COOLING WATER
NH₃ VAPOR
NH₃ LIQUID
NH₃ VAPORIZER
MAKE-UP WATER

Figure 6-5. Schematic Flow Sheet of the CDL/VITOK NO_x Removal Process (Ref. 6-8).

kg/Mg of nitric acid (5.5 lbs/ton). A flow diagram of their abatement equipment is shown in Figure 6-6 (Reference 6-10). It consists of a cooler attached to the nitric acid absorption tower, and a bleacher from which any effluent gases are recycled to the absorption tower. As a result of adding the NO_x control process the concentration of the product acid dropped from 65 percent to 51 to 57 percent.

6.1.3.2 Extended Absorption

The extended absorption process basically consists of a second absorption column to which the tail gas from the nitric acid plant is sent. The NO_x is absorbed by water and forms nitric acid, which increases the acid yield. Extended absorption can be added in conjunction with pressurizing the tail gas upstream of the tower or chilling the absorbent in the tower. However, neither of these options is a necessary part of the absorption process.

This process is offered by several licensors, including J. F. Pritchard (Grande Paroisse process), D. M. Weatherly, Chemico, Uhde and C and I Gridler (CoFaz process). The economics of the process generally require the inlet pressure at the absorber to be at least 758 kPa (110 psia). Also, cooling is usually required if the inlet NO_x concentration is above 3000 ppm (Reference 6-6). There is no liquid or solid effluent from extended absorption; the weak acid from the secondary absorber is recycled to the first absorber, increasing the yield of nitric acid. In some cases, extended absorption can be used in conjunction with catalytic tail gas treatment (see Section 6.1.3.4).

Figure 6-7 shows a process flow diagram for the Grande Paroisse process, which is representative of extended absorption processes. Off-gas from the existing absorber flows into the secondary, or Grande Paroisse absorber. The tail gas from the secondary absorber goes to an existing tail-gas heater before being vented to the atmosphere or passing through a catalytic reduction unit. The liquid effluent is returned to the primary absorber to become part of the acid product.

More than 15 extended absorption plants (by various licensors) are operating in the United States. In cases where the off-gas must be compressed before going to the secondary absorber, or where refrigeration is used, maintenance requirements are increased. Power recovery by an air compressor/tail-gas expander is usually employed when a pressurized absorber is used.

6.1.3.3 Wet Chemical Scrubbing

Wet chemical scrubbing uses liquids, such as alkali hydroxides, ammonia, urea and potassium permanganate to convert NO_2 to nitrates and/or nitrites by chemical reaction. Also, scrubbing may be done with water or with nitric acid. Several of these processes are described below.

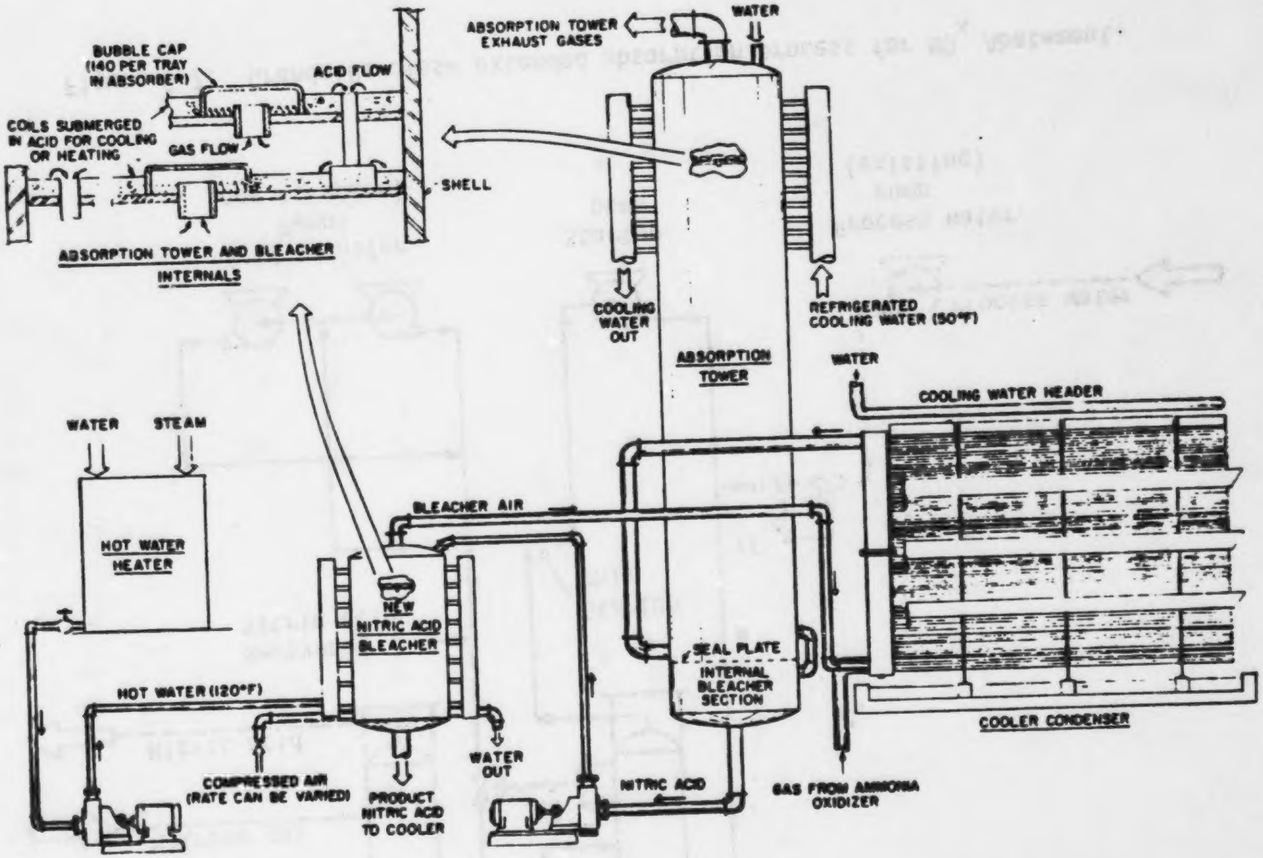
BUBBLE CAP (140 PER TRAY IN ABSORBER)
ACID FLOW
COILS SUBMERGED IN ACID FOR COOLING OR HEATING
GAS FLOW
SHELL
ABSORPTION TOWER AND BLEACHER INTERNALS
ABSORPTION TOWER EXHAUST GASES
WATER
COOLING WATER OUT
REFRIGERATED COOLING WATER (50°F)
ABSORPTION TOWER
WATER
COOLING WATER HEADER
WATER
STEAM
HOT WATER HEATER
BLEACHER AIR
NEW NITRIC ACID BLEACHER
SEAL PLATE
INTERNAL BLEACHER SECTION
COOLER CONDENSER
HOT WATER (120°F)
COMPRESSED AIR (RATE CAN BE VARIED)
PRODUCT NITRIC ACID TO COOLER
WATER OUT
NITRIC ACID
GAS FROM AMMONIA OXIDIZER

Figure 6-6. TVA chilled absorption process (Reference 6-10).

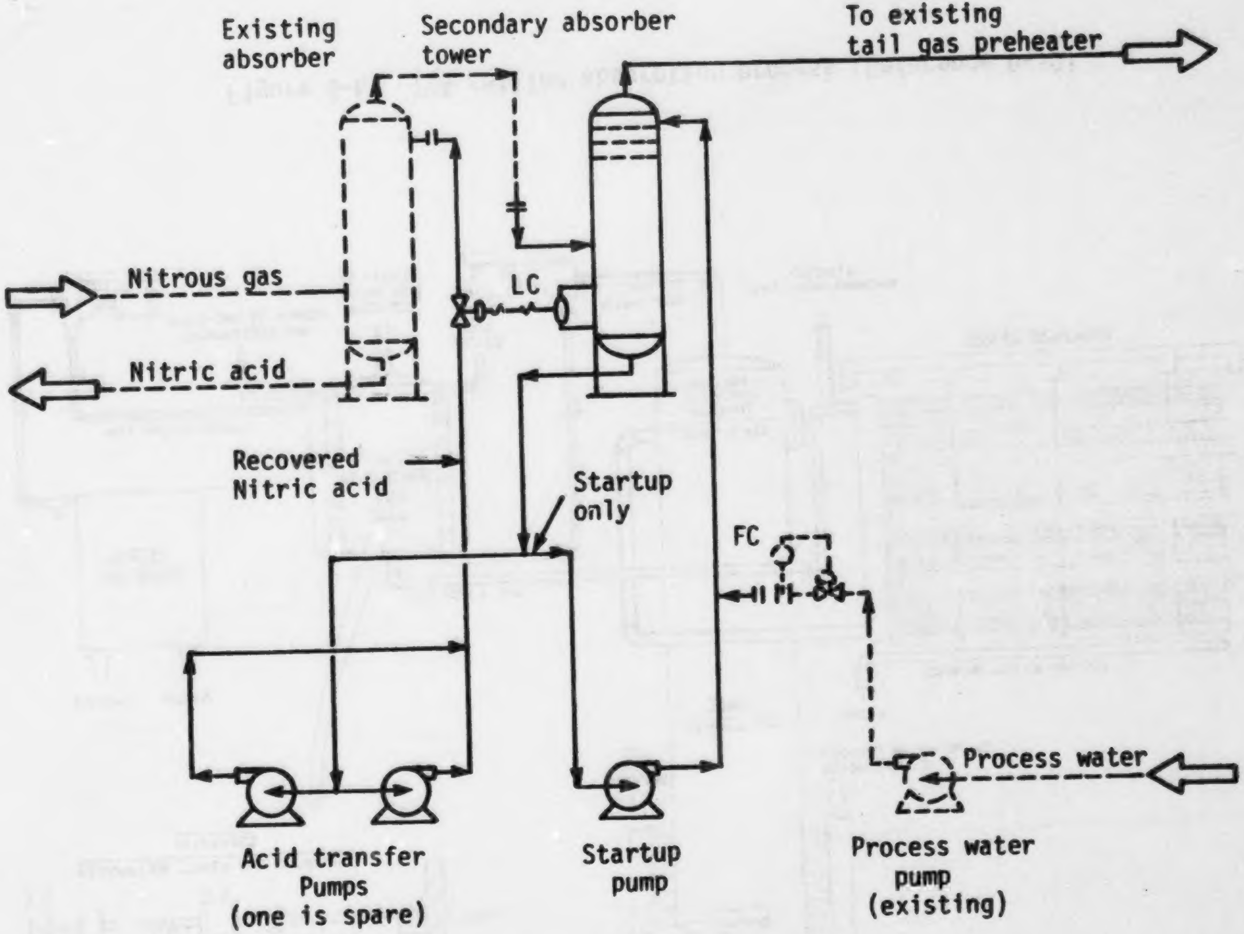
Existing absorber
Secondary absorber tower
To existing tail gas preheater
Nitrous gas
Nitric acid
LC
Recovered Nitric acid
Startup only
FC
Process water
Acid transfer Pumps (one is spare)
Startup pump
Process water pump (existing)

Figure 6-7. Grande Paroisse extended absorption process for NO_x Abatement.

Urea Scrubbing

This process is offered by two licensors: MASAR, Inc. and Norsk Hydro. The mechanisms given below have been proposed for this process (Reference 6-11).

$$HNO_2 + CO(NH_2)_2 \rightleftarrows N_2 + HNCO + 2H_2O \qquad (6\text{-}4)$$

$$HNCO + HNO_2 \rightleftarrows N_2 + CO_2 + H_2O \qquad (6\text{-}5)$$

$$HNCO + H_2O + H^+ \rightleftarrows NH_4^+ + CO_2 \qquad (6\text{-}6)$$

When the concentration of nitric acid is low, reaction (6-6) predominates so that the overall reaction is

$$HNO_2 + CO(NH_2)_2 + HNO_3 \rightleftarrows N_2 + CO_2 + NH_4NO_3 + H_2O \qquad (6\text{-}7)$$

As shown in reaction (6-7), half the nitrogen in the reaction will form NH_4NO_3, a valuable by-product, and half will form N_2, a nonpolluting species.

The MASAR process is shown in Figure 6-8. A three-stage absorption column is used with gas and liquid chillers on the feed gas and recirculated solvents. The process as described by MASAR, Inc., (Reference 6-12) is given below.

The MASAR process, as applied to nitric acid plants, takes the tail gas from the exit of the absorption tower and passes it to a gas chiller where it is cooled. During this cooling operation, condensation occurs with the formation of nitric acid. This chilled gas and condensate passes into Section A of the MASAR absorber. Meanwhile, the normal feedwater used in the nitric acid plant absorption tower is chilled in Section C of the MASAR absorber and is then fed to Section A of the MASAR absorber, where it flows down through the packing countercurrent to the incoming chilled tail gas to scrub additional NO_x from the tail gas. This scrubbing water is recirculated through a chiller to remove reaction heat and then this weak nitric acid stream is fed to the nitric acid plant absorber to serve as its feedwater.

The tail gas then passes into Section B of the MASAR absorber where it is scrubbed with a circulating urea-containing solution. A urea/water solution is made up in a storage tank and metered into the recirculating system at a rate necessary to maintain a specified minimum urea residual content. As the solution scrubs the tail gases, both nitric acid and nitrous acids are formed, and the urea in the solution reacts with the nitrous acid to form $CO(CO_2)$, N_2, and H_2O. As the solution is circulated, the nitric acid content rises and some of the urea present hydrolyzes and forms some ammonium nitrate. To maintain the system in balance, some of the circulated solution is withdrawn. The recirculated solution is also pumped through a chiller to remove the heat of reactions and to maintain the desired process temperature in Section B.

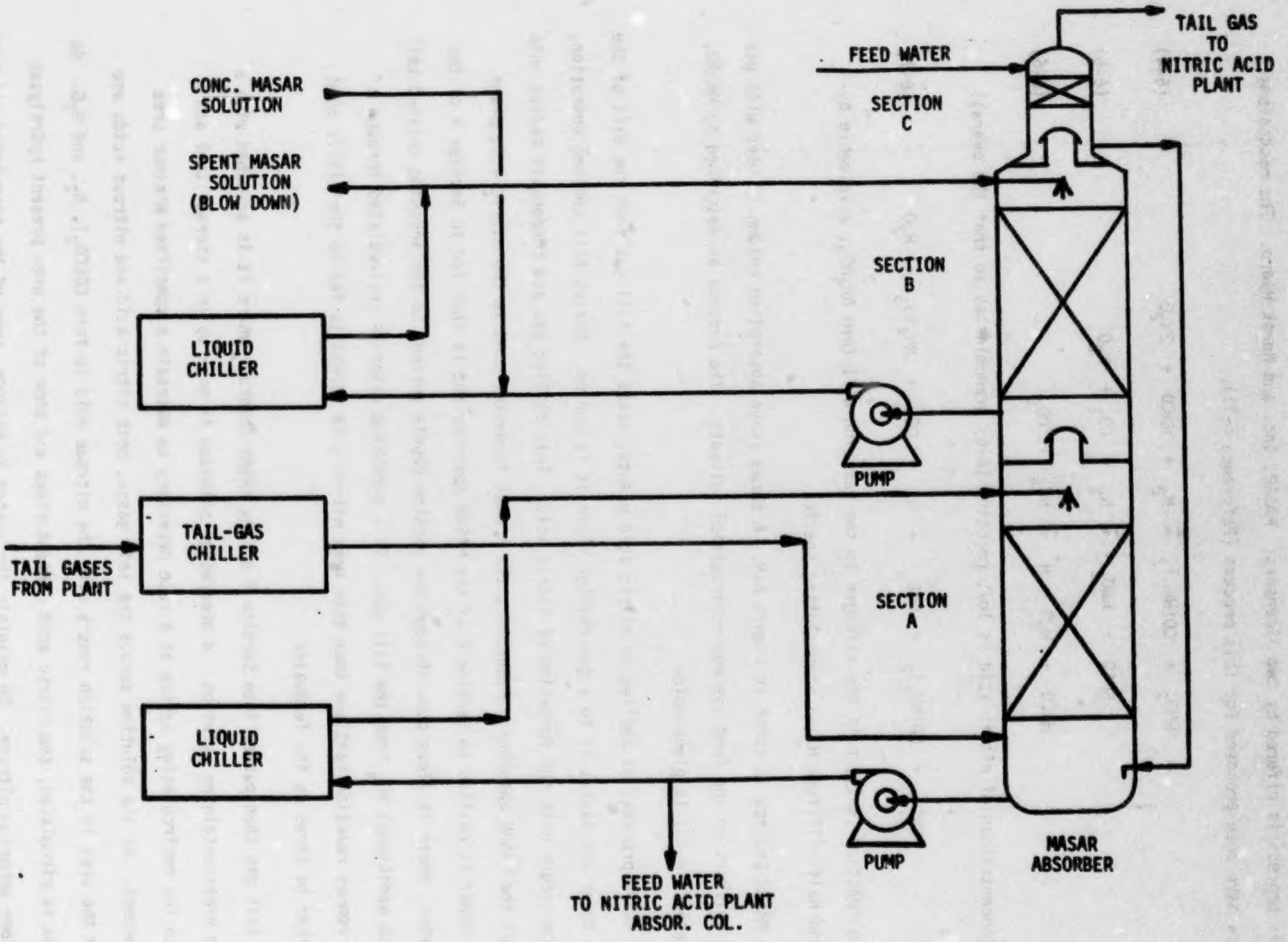
TAIL GAS TO NITRIC ACID PLANT
FEED WATER
SECTION C
SECTION B
SECTION A
MASAR ABSORBER
PUMP
PUMP
CONC. MASAR SOLUTION
SPENT MASAR SOLUTION (BLOW DOWN)
LIQUID CHILLER
TAIL-GAS CHILLER
LIQUID CHILLER
TAIL GASES FROM PLANT
FEED WATER TO NITRIC ACID PLANT ABSOR. COL.

Figure 6-8. Flow diagram of the MASAR process (Reference 6-12).

The tail gases then pass into Section C where they are again scrubbed by the feedwater stream that is used, ultimately, as the nitric acid plant absorption tower feedwater. The tail gases then leave the MASAR absorber and pass on to the normally existing mist eliminator and heat exchanger train of the nitric acid plant. The cooling medium used in the gas chiller can be liquid ammonia. The vaporized ammonia is subsequently used as the feed to the plant ammonium nitrate neutralizer. For non-ammonia nitrate producers, mechanical refrigeration could be used or the ammonia vapor can be used in the nitric acid converter directly.

The MASAR process has been reported to reduce NO_x emissions from 4000 ppm to 100 ppm. The process could technically be designed for no liquid effluent. In practice, however, liquid blowdown of 16 kg/h (35 lb/hr) of urea nitrate in 180 kg/h (396 lb/hr) of water is estimated for a 320 Mg of acid/day (350 tons/day) plant (Reference 6-12).

A MASAR unit installed in 1974 for Illinois Nitrogen Corporation on a 320 Mg/d plant regularly operates with between 100 and 200 ppm of NO_x in the tail gas. According to the Illinois Nitrogen plant manager (Reference 6-13), inlet NO_x concentrations to the MASAR unit are approximately 3500 ppm and outlet concentrations are between 200 and 400 ppm. The Illinois Environmental Protection Agency has tested this unit, using Method 7, with reproducible results of 57 ppm average emissions. The unit is reported to operate with good reliability and has increased the net product recovered.

The Norsk Hydro process was developed by Norsk Hydro A/S, the Norwegian state-owned power generating authority and fertilizer and chemical manufacturer, to reduce NO_x emissions from 1525 ppm to 850 ppm. The modifications were made to an older, atmospheric pressure plant and two more recent medium-pressure plants (300 and 500 kPa) (44 to 72 psia). Basically, the last absorption towers in the process streams of the older plant were modified to contact the tail gases from all three plants with urea solution and nitric acid. The result was a net 44 percent reduction in NO_x emissions, as given above. On a plant-wide basis, 10.4 kg of ammonium nitrate are produced per Mg of nitric acid (20.8 lb/ton) (Reference 6-11).

Norsk Hydro has also used urea addition on three plants producing a total of 5 Gg/d (5500 tons/day) of prilled NPK fertilizers. This method was used to control NO_x emissions for lower-grade phosphate rock. Nitrous oxide is evolved when nitric and nitrous acid oxidizes impurities in the rock such as sulphides and organic material. The addition of urea to the phosphate rock digester tends to reduce NO_x emissions to 2.5 kg/Mg (5 lb/ton) phosphate from levels as high as 40 kg NO_x per Mg phosphate (80 lb/ton) by adding 5 to 10 kg urea per Mg phosphate rock (10 to 20 lb/ton) (Reference 6-11).

Ammonia Scrubbing (Goodpasture Process)

Goodpasture, Inc. of Brownfield, Texas is the licensor of a process developed in 1973 in order for its Western Ammonia Corporation nitrogen complex in Dimitt, Texas to meet a 600 ppm maximum NO_x effluent imposed by the Texas Air Control Board. The process which was developed is suitable to retrofit existing plants for reduction of an inlet concentration of 10,000 ppm to within the 1.5 kg NO_2/Mg acid (~210 ppm) standards set for new nitric acid plants.

The process flow diagram for this process is shown in Figure 6-9. Feed makeup streams to this process are ammonia and water with ammonium nitrate produced as a byproduct. The total process is conducted in a single packed contact absorption tower with three sections operated in a co-current flow. Goodpasture states that the key to successful operation is the process' capability to minimize the formation of ammonium nitrite and to oxidize the ammonium nitrite which does form to ammonium nitrate.

The Goodpasture process consists of three distinct sections. The first is a gas absorption and reaction section operating on the acidic side, the second is a gas absorption and reaction section operating on the ammoniacal side, and the third is principally a mist collection and ammonia recovery step.

In the first section, a significant portion of the oxides of nitrogen react to form nitric acid which maintains the acidic condition in this section. The nitric acid formed reacts with the free ammonia content of the solution from the ammoniacal section to form ammonium nitrate — a portion reacting in the acidic section, and a portion reacting in the ammoniacal section. The feed solution to the acidic section is the product solution from the ammoniacal section. The ammonium nitrite content of this solution is oxidized to ammonium nitrate by the acidic conditions existing in this first section. The product solution from the Goodpasture process is withdrawn from this acidic section.

In the second, or ammoniacal contacting, section the remainder of the oxides of nitrogen react to form ammonium nitrate and ammonium nitrite; the proportion of each being dependent on the oxidation state of the oxides of nitrogen in the gas phase. Ammonia is added to the circulating solution within this section to maintain the pH at a level of 8.0 to 8.3. The liquid feeds to this section are the product solution from the mist collection section, and a portion of the acidic solution from the first section.

The third section is incorporated principally to collect the mist, and any ammonium nitrate or ammonium nitrite aerosols which form in the first two sections. In addition, any free ammonia

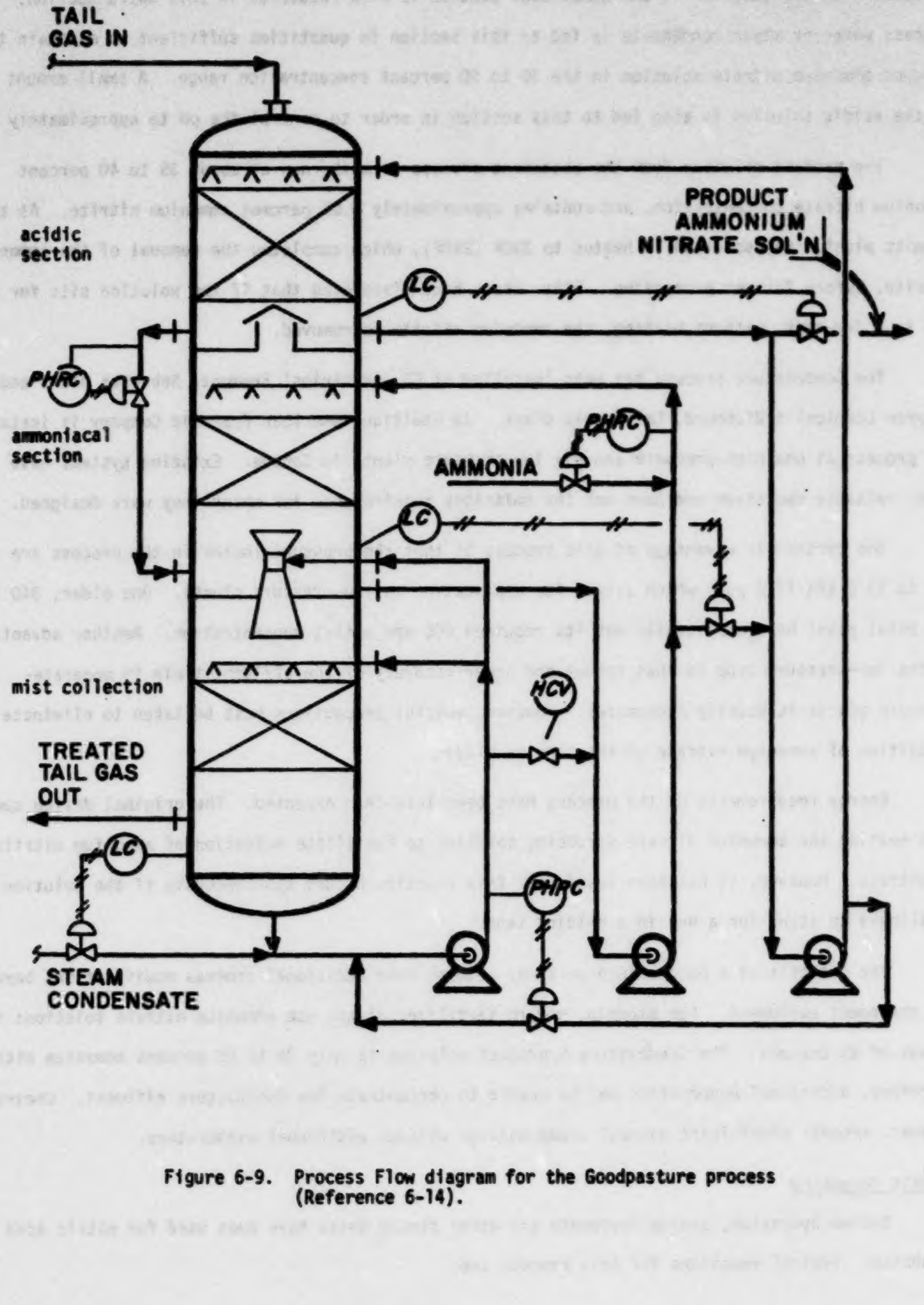
TAIL GAS IN
acidic section
PRODUCT AMMONIUM NITRATE SOL'N
LC
PHRC
ammoniacal section
PHRC
AMMONIA
LC
mist collection
HCV
TREATED TAIL GAS OUT
LC
PHRC
STEAM CONDENSATE

Figure 6-9. Process Flow diagram for the Goodpasture process (Reference 6-14).

stripped from the solution in the ammoniacal section is also recovered in this third section. Process water or steam condensate is fed to this section in quantities sufficient to maintain the product ammonium nitrate solution in the 30 to 50 percent concentration range. A small amount of the acidic solution is also fed to this section in order to control the pH to approximately 7.0.

The product solution from the abatement process is withdrawn at about 35 to 40 percent ammonium nitrate concentration, and contains approximately 0.05 percent ammonium nitrite. At the Dimmitt plant, this solution is heated to 390K (240F), which completes the removal of the ammonium nitrite, before further processing. Other users have discovered that if the solution sits for a day in a day-tank, without heating, the ammonium nitrite is removed.

The Goodpasture process has been installed at CF Industries' Fremont, Nebraska plant and Chevron Chemical's Richmond, California plant. In addition, American Cyanamid Company is installing the process at one high-pressure and six low-pressure plants in Canada. Existing systems have given reliable operation and have met the emissions requirements for which they were designed.

One particular advantage of this process is that the pressure losses in the process are only 6.8 to 13.0 kPa (1-2 psi) which allows its application to low-pressure plants. One older, 340 kPa (49 psia) plant has consistently met its required 400 ppm outlet concentration. Another advantage of the low-pressure drop is that reheat and power recovery of the effluent train in moderate-pressure plants is usually economical. However, special precautions must be taken to eliminate deposition of ammonium nitrate on the turbine blades.

Energy requirements of the process have been less than expected. The original design specified heating the ammonium nitrate scrubbing solution to facilitate oxidation of ammonium nitrite to nitrate. However, it has been found that this reaction occurs spontaneously if the solution is allowed to stand for a day in a holding tank.

The retrofit of a Goodpasture unit may require some additional process modifications beyond the abatement equipment. For example, modern fertilizer plants use ammonium nitrate solutions in excess of 85 percent. The Goodpasture byproduct solution is only 35 to 55 percent ammonium nitrate; therefore, additional evaporators may be needed to concentrate the Goodpasture effluent. Chevron; however, reports significant overall steam savings without additional evaporators.

Caustic scrubbing

Sodium hydroxide, sodium carbonate and other strong bases have been used for nitric acid scrubbing. Typical reactions for this process are:

$$2NaOH + 3NO_2 \rightleftarrows 2NaNO_3 + NO + H_2O \qquad (6\text{-}8)$$

$$2NaOH + NO + NO_2 \rightleftarrows 2NaNO_2 + H_2O \qquad (6\text{-}9)$$

A caustic scrubbing system was installed at a Canadian nitric acid plant in the late 1950's (Reference 6-15). However, disposal of the spent solution is a serious water pollution problem, and the concentrations of the salts are too low for economic recovery. There have been no recent installations of this process.

Potassium Permanganate Scrubbing

Another potential chemical for scrubbing solutions is potassium permanganate. The Carus Chemical Company (a large producer of potassium permanganate) has developed a process for potassium permanganate solution scrubbing of NO_x. However, in the process, permanganate is reduced to manganate, which must be electrolytically oxidized. The cost for the electrolysis, as well as the permanganate make up cost, makes the process uneconomical. This process has not been installed at any nitric acid plant in this country. Two plants are in operation in Japan, but no cost or user information is available.

6.1.3.4 Catalytic Reduction

This section describes two different catalytic reduction processes. They are nonselective catalytic reduction and selective catalytic reduction.

Nonselective Catalytic Reduction

In nonselective catalytic absorption, methane or hydrogen reacts with the NO_x and oxygen in the tail gas to form N_2, H_2O, and CO_2. A schematic of a typical catalytic reduction unit is shown in Figure 6-10. The reactions (given in Section 3.3.2.4) in the abater are exothermic; and careful temperature control is necessary for effective operation. The controls needed for operation as a decolorizer are much less stringent.

Catalytic reduction units for decolorization and power recovery are used in about 50 nitric acid plants in the United States. Many plants use natural gas for the reducing agent because of its easy availability and low cost.* Some plants use hydrogen. When natural gas is used, the tail gas must be preheated to about 753K (900F) to ensure ignition. A preheat temperature as low as 423K (300F) is sufficient to ignite hydrogen.

Catalytic reduction is highly exothermic. The temperature rise for the reaction with methane is about 128K (230F) for each percent oxygen burnout; with hydrogen it is about 150K (270F). For

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*Relative to hydrogen this is still true; however, the economics of using natural gas have greatly changed in the last three years.

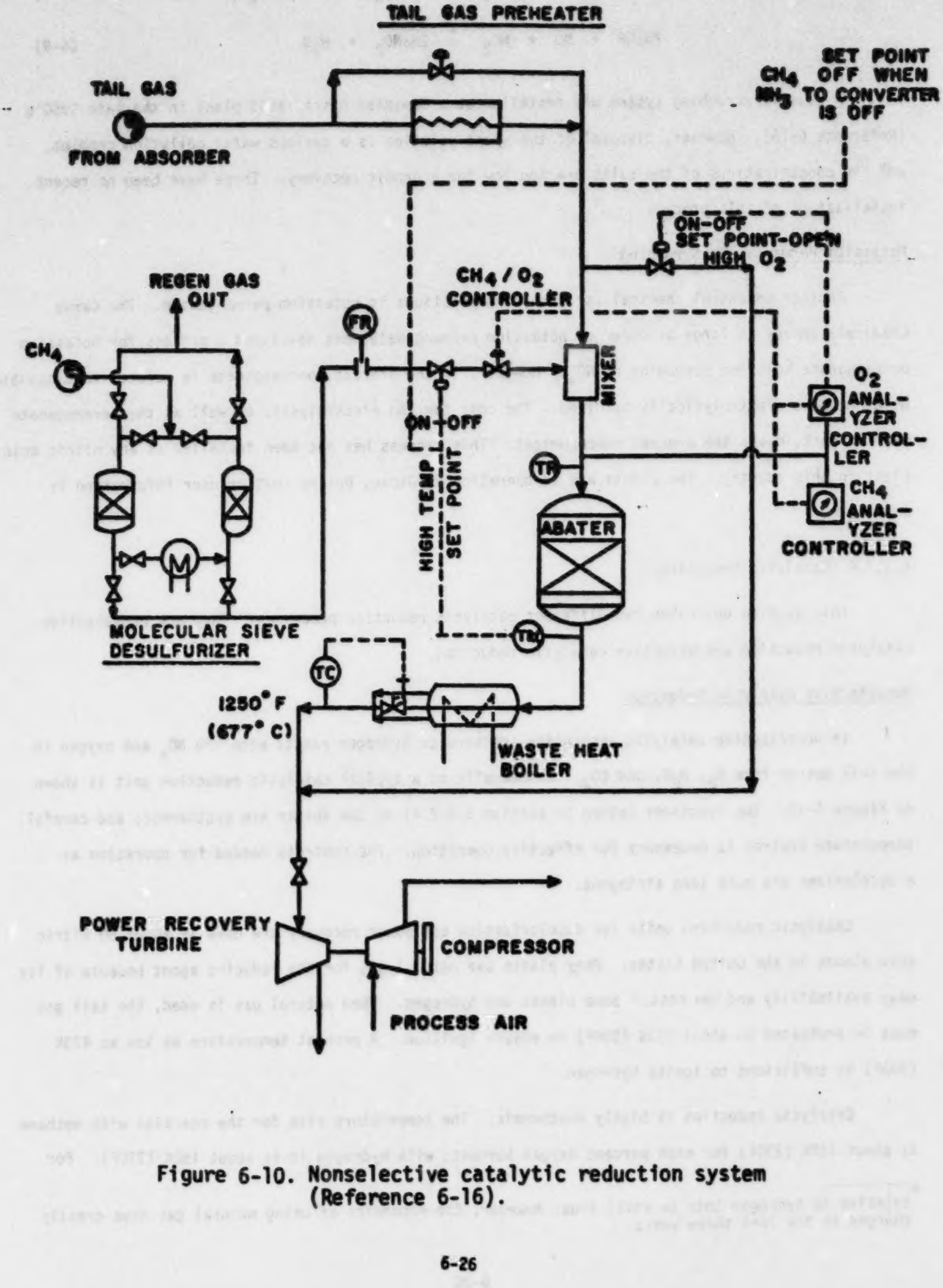

TAIL GAS PREHEATER
TAIL GAS
FROM ABSORBER
CH_4
SET POINT
OFF WHEN
NH_3 TO CONVERTER
IS OFF
ON-OFF
SET POINT-OPEN
HIGH O_2
REGEN GAS
OUT
CH_4 / O_2
CONTROLLER
CH_4
FR
MIXER
O_2
ANAL-
YZER
CONTROL-
LER
ON-OFF
HIGH TEMP
SET POINT
TR
CH_4
ANAL-
YZER
CONTROLLER
ABATER
M
MOLECULAR SIEVE
DESULFURIZER
TR
TC
1250° F
(677° C)
WASTE HEAT
BOILER
POWER RECOVERY
TURBINE
COMPRESSOR
PROCESS AIR

Figure 6-10. Nonselective catalytic reduction system (Reference 6-16).

decolorization, the outlet temperature is ordinarily limited to 923K (1,200F), the maximum temperature limit of turboexpanders with current technology. Increased power recovery may justify adding sufficient methane to reach the temperature limit of the turbine.

The tail gas must be preheated to 753K (900F) to insure ignition when methane is used as the reducing agent. Outlet temperatures would reach 1,088K and 1,138K (1,500F and 1,590F) for 2 and 3 percent oxygen burnout, respectively. These temperatures compare to the 923K (1,200F) maximum temperature limit for single-stage operation. The oxygen in the tail gas cannot exceed 2.8 percent to remain within the temperature limit of the catalyst. Cooling must therefore be provided to meet the turboexpander limit. Older turbines may have even lower temperature limitations.

A somewhat cheaper but less successful alternative is two-stage reduction for abatement. One system involves two reactor stages with interstage heat removal (Reference 6-17). Another two-stage system for abatement involves preheating 70 percent of the feed to 753K (900F), adding fuel, and passing the mixture over the first-stage catalyst. The fuel addition to the first stage is adjusted to obtain the desired outlet temperature. The remaining 30 percent of the tail gas, preheated to only 393K (250F), is used to quench the first stage effluent. The two streams plus the fuel for complete reduction are mixed and passed over the second-stage catalyst; the effluent passes directly to the turboexpander. This system avoids high temperatures and the use of coolers and waste heat boilers (References 6-18, 6-19, and 6-20).

Honeycomb ceramic catalysts have been employed in two-stage abatement, with hourly gas-space velocities of about 100,000 volumes per hour per volume in each stage (Reference 6-21).

Nonselective catalyst systems are offered by D. M. Weatherly, C & I Girdler and Chemico. These systems are not as popular as NO_x control methods because of rising fuel costs.

Two or three plants are known to have installed single-stage nonselective abaters. They are believed to have been designed for natural gas. As noted above, oxygen concentration cannot exceed about 2.8 percent. The reactors must be designed to withstand 1,088K to 1,118K (1,500F to 1,550F) at 790 to 930 kPa, which requires costly refractories or alloys. Ceramic spheres are used as catalyst supports, at hourly gas space velocities up to 30,000 volumes per hour per volume. One company reports that they have been able to maintain NO_x levels of 500 ppm or less over an extended period of time. Operation close to 300 ppm might be attainable. On a plant scale, the effluent gas must be cooled by heat exchange or quenched to meet the temperature limitation of the turbine. It may be practical to use a waste heat boiler to generate steam.

Commercial experience with single-stage catalytic abaters has been modestly satisfactory, but two-stage units operating on natural gas have not been as successful. Two-stage units designed for abatement have frequently achieved abatement for periods of only a few weeks, at which point declining catalyst activity results in increasing NO levels. Recent data indicate that successful abatement can be maintained for somewhat longer periods. Units that no longer abate NO_x emissions can, however, continue to serve for energy recovery and decolorization.

The success of single-stage abaters compared to the limited success of two-stage units may result from the following factors: the catalyst is in a reducing atmosphere, the temperatures are higher, and spherical rather than honeycomb catalyst supports are used. It has not been practical to change catalyst type in two-stage units because the reactors designed for a space velocity of 100,000 volumes per hour per volume would be too small to accommodate a spherical catalyst, which effectively removes NO_x at a space velocity of about 30,000. The failure of the honeycomb catalyst in NO_x reduction compared to its success in decolorization may reflect that reaction kinetics make it much more difficult to reduce NO than NO_2.

Fuel requirements for nonselective abatement with methane are typically 10 to 20 percent over stoichiometric. Some hydrocarbons and CO appear in the treated tail gas. Furthermore, not all methane is converted in decolorization reduction units. Less surplus fuel is required when hydrogen is used.

Selective Catalytic Reduction

In selective catalytic reduction, ammonia is reacted with the NO_x to form N_2. No large temperature rise occurs for ordinary operating conditions, so no waste heat or steam is generated. The catalyst used in selective abatement units is platinum on a honeycomb support. Many catalytic systems are installed between the expander and the economizer heat exchanger, and operate at ambient pressure. This lack of pressure sensitivity is an advantage for retrofitting older low-pressure nitric acid plants. It is important to control the temperature between 483K and 543K (410F and 518F) because above 543K, ammonia may oxidize to form NO_x; below 483K, it may form ammonium nitrate.

Gulf Oil Chemicals is the main licensor of selective catalytic abaters in North America. They have eight systems onstream, and two more planned. Of these systems, nine operate at ambient pressure, and one operates at 590 kPa (86 psia). Many of these catalyst beds also use a molecular sieve for NO_2 adsorption to promote the reaction with ammonia.

Uhde licenses the BASF selective catalyst process and recommends it for tail gas treatment of 600 kPa (87 psig) nitric acid plants.

User experience with these processes has been good. Catalyst lifetimes of over 2 years have been reported, and expected lifetime is 5 to 10 years. Catalytic processes have also been used to supplement chilled absorption units when they have failed to meet emission limits.

6.1.3.5 Molecular Sieve Adsorption

The main equipment in a molecular sieve adsorption system is in the form of a two-section packed bed. The first section is packed with a desiccant, since the NO_x adsorption sieve material works best on a dry gas. The second section contains the material which acts as nitrous oxide oxidation catalyst and NO_x adsorber.

Figure 6-11 is a schematic of a molecular sieve system added to an existing nitric acid plant. NO_x removal is accomplished in a fixed bed adsorption/catalyst system. The water-saturated nitric acid plant absorption tower overheat stream is chilled to 283K (50F), the exact temperature level being a function of the NO_x concentration in the tail-gas stream. It is then passed through a mist eliminator to remove entrained water and acid mist. The condensed water, which absorbs some of the NO_2 in the tail gas to form a weak acid, is collected in the mist eliminator and either recycled to the absorption tower or sent to storage. The tail gas then passes through a molecular sieve bed where the special properties of the NO_x removal bed material results in the catalytic conversion of nitric oxide (NO) to nitrogen dioxide (NO_2). This occurs in the presence of the low concentrations of oxygen typically present in the tail-gas stream. Nitrogen dioxide is then selectively adsorbed.

Regeneration is accomplished by thermally cycling (or swinging) the adsorbent/catalyst bed after it completes its adsorption step and while it contains a high adsorption loading of NO_2. An oil-fired heater is used to provide heat for regeneration. The required regenerator gas is obtained by using a portion of the treated tail-gas stream for desorption of the NO_2. This NO_2-loaded gas is recycled to the nitric acid plant absorption tower. The pressure drop in the molecular sieve averages 34 kPa (5 psi) and NO_x outlet concentration averages 50 ppm (Reference 6-22).

This process has been applied to three plants in the United States (Reference 6-6). Tables 6-2 and 6-3 show the performance of the system at two installations. The commercial name for the process is the Purasiv N process. The unit at the 50 Mg/d (55 tons/day) acid plant of Hercules, Inc. started up in 1974. Abatement ranged from 95.9 to 98.7 percent averaged over individual cycles and was highest at the beginning of a cycle (Reference 6-23). The U.S. Army Holston Purasiv N unit was started up in August 1974, but has been inoperable for several years.

Both plants have dual-unit NO_x adsorbers, operating on a 4 hour adsorption, 4 hour regeneration cycle (Reference 6-22). Initial reports on the operation were very favorable; the effluent standards were met, and the sieve showed no noticeable deterioration after 6 months. One sieve was damaged by accidental acid back-up, however, and did not achieve the expected 50 ppm outlet concentration.

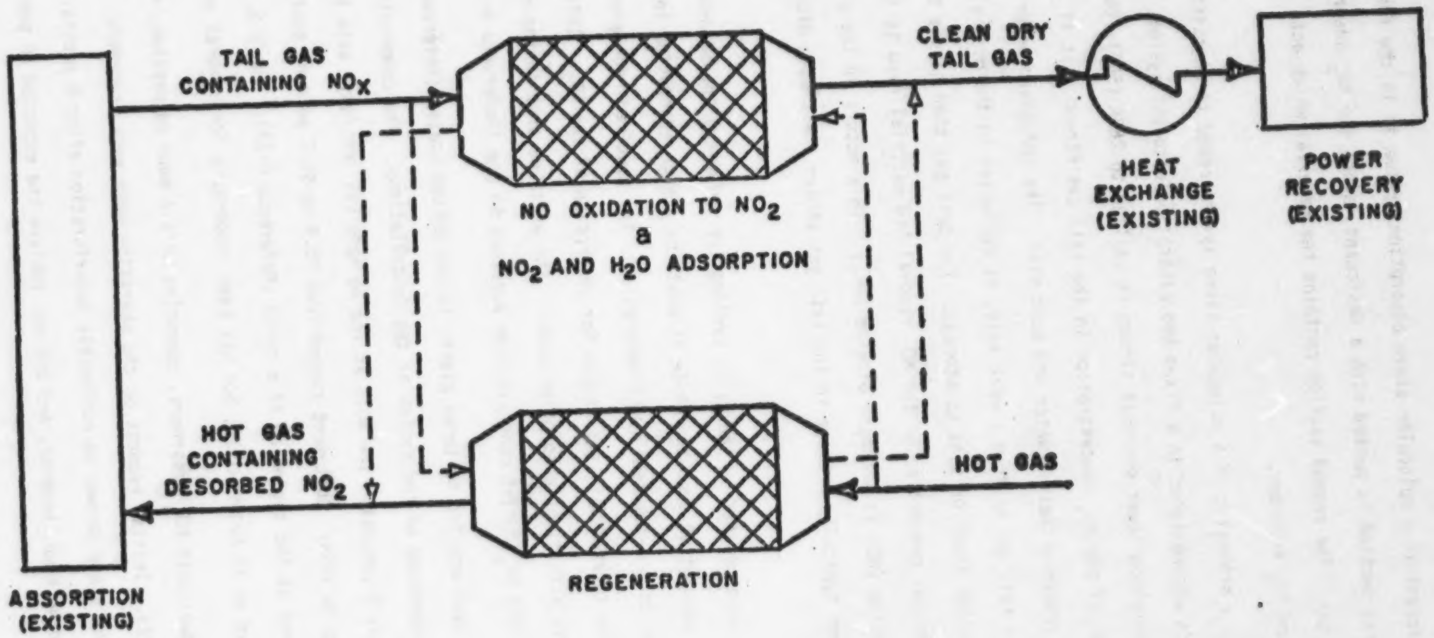

TAIL GAS
CONTAINING NO_X
CLEAN DRY
TAIL GAS
NO OXIDATION TO NO_2
&
NO_2 AND H_2O ADSORPTION
HEAT
EXCHANGE
(EXISTING)
POWER
RECOVERY
(EXISTING)
HOT GAS
CONTAINING
DESORBED NO_2
HOT GAS
REGENERATION
ABSORPTION
(EXISTING)

Figure 6-11. Molecular sieve system (Reference 6-22).

TABLE 6-2. PERFORMANCE OF HERCULES PURASIV N UNIT DURING THREE DAY RUN (REFERENCE 6-24)

	May 16	May 27	May 28
NO_x in Effluent			
Average, ppm	2	2	5
Range, ppm	0-6	0-7	0-25
NO_x in Feed			
Average, ppm	2,600	2,400	2,450
Range, ppm	2,000-3,000	2,300-2,500	2,300-2,500
Average Gas Flow			
Tail gas flow, Nm^3/s[a]	2.29	2.19	2.17
Recycle gas flow, Nm^3/s	0.45	0.45	0.45
Total gas flow, Nm^3/s	2.74	2.64	2.62

[a] $1 Nm^3/s = 2118.9$ scfm

TABLE 6-3. PERFORMANCE OF U.S. ARMY-HOLSTON PURASIV N UNIT DURING THREE DAY RUN (REFERENCE 6-24) (PLANT LARGELY DISMANTLED)

	August 17	August 18	August 19
NO_x in Effluent			
Average, ppm	<1	6	7
Range, ppm	0-2	0-30	0-30
NO_x in Feed			
Average, ppm	4,100	3,700	3,900
Range, ppm	3,000-5,700	3,500-4,400	2,500-4,700
Average Gas Flow			
Tail gas flow, Nm^3/s[a]	2.08	2.08	2.08
Recycle gasflow, Nm^3/s	0.52	0.52	0.52
Total gas flow, Nm^3/s	2.60	2.60	2.60

[a] 1 Nm^3/s = 2118.9 scfm

The process has been successful in meeting emission standards. The principal criticisms have been high capital and energy costs, and the problems of coupling a cyclic system to a continuous acid plant operation. Furthermore, molecular sieves are not considered as state-of-the-art technology.

6.1.4 Costs

The most recent cost and energy utilization comparisons of the various abatement processes are given in Tables 6-4 and 6-5 (Reference 6-6). Direct comparison of these data is rather difficult since not all the side effects, such as changes in plant yield, and the degree of abatement, are described.

Chilled Absorption

The cost figures in Table 6-4 for the CDL/VITOK process are in agreement with data provided by Reference 6-25. According to Reference 6-10, the bottom line costs for the chilled absorption process used by the TVA is \$2.09/Mg (\$1.90/ton) of acid, which includes \$0.14/Mg (\$0.13/ton) credit for additional product, 8 kWh and 85 kg steam per Mg acid (170 lb/ton). This cost is higher than the \$1.74 Mg (\$1.58/ton) given in Table 6-4 and does not include the reduction in capacity caused by the reduction in the nitric acid concentration.

Extended Absorption

The Grande Paroisse process is capital intensive; therefore, costs may be dominated by the assumptions made to calculate return on investment and depreciation. The figures in Table 6-4 reflect a 20 percent return on capital. The Grande Paroisse literature shows cost of \$0.98 to \$1.13 per Mg (\$0.89 to \$1.03/ton) but does not consider a return on investment cost.

Even with high capital cost and unfavorable cost of capital, extended absorption is competitive with other processes. It has low maintenance costs and low energy requirements.

Wet Chemical Scrubbing

The economics and energy use of two wet scrubbing processes, MASAR, urea scrubbing, and Goodpasture, ammonia scrubbing, are given in Tables 6-4 and 6-5. Costs for the Norsk Hydro process would be similar if applied to a new plant. Capital cost for the Goodpasture process are estimated as \$425,000 for a 270 Mg/d (300 tons/day) plant (Reference 6-26). No costs estimates are available for potassium permanganate and caustic scrubbing since they are not in general use.

TABLE 6-4. CAPITAL AND OPERATING COSTS FOR DIFFERENT NO_x ABATEMENT SYSTEMS IN A 270 Mg/d NITRIC ACID PLANT (References 6-6 and 6-26)[a]

	Catalyst Reduction	Molecular Sieve	Grande Paroisse	CDL/ Vitok	Masar	Goodpasture
Capital Investment,[b] ($)	1,384,000	1,200,000	1,000,000	575,000	663,000	425,000
Royalty	--	--	Included	None	Fee	51,000
Operating Labor, (hr/yr)	360	360	360	360	360	360
($/yr)	2,200	2,200	2,200	2,200	2,200	2,200
Maintenance Labor,	315	315	315	315	315	315
($/yr)	2,200	2,200	2,200	2,200	2,200	2,200
Labor Overhead (incl. fringe benefits & supervision, $/yr)	4,400	4,400	4,400	4,400	5,975	4,400
Catalyst or Molecular Sieve	77,800	45,600	--	--	--	--
Cooling Water, (l/min)	--	1,892	1,135	3,861	--	114
($/yr)	--	7,330	4,420	14,980	--	440
Steam, (kg/hr)	(7,182)	113	--	324	594	--
($/yr credit)	(387,590)	6,120	--	17,500	32,070	--
Electricity, (kWh)	128	322	90	265	20	45
($/yr)	20,890	52,550	14,690	43,250	3,260	7,340
Boiler Feed Water, (l/min)	132					--
($/yr)	12,850	--	--	--	--	--
Fuel, MW	8.3	0.6	--	--	--	--
($/yr)	465,120	32,640	--	--	--	--
Nitric Acid, (Mg/day)	--	(6.0)	(5.4)	(5.4)	(4.8)	--
($/yr)	--	(112,200)	(102,000)	(102,000)	(89,760)	--
Urea, (Mg/day)	--	--	--	--	1.24[c]	--
($/yr)					74,528	--
Ammonium Nitrate, (Mg/day)					(1.13)	(11.8)
($/yr)					(24,500)	(422,000)
Depreciation (11-yr. life)	125,900	109,090	90,910	52,300	60,300	38,640
Return on Investment (@ 20%)	276,800	240,000	200,000	115,000	132,600	85,000
Taxes & Insurance (@ 2%)	27,700	24,000	20,000	11,500	13,260	8,500
Total Annual Cost, ($/yr)	628,270	413,930	236,780	161,330	195,708	(42,290)
Annual Cost, ($/Mg)	6.79	4.48	2.56	1.74	2.12	(0.46)

[a] This table is given in Appendix A in English units.

[b] Investment estimates exclude interest during construction, owners expenses, and land costs.

[c] Include credit for 0.0017 Mg of urea/Mg of nitric acid produced present in the spent solution (D.SITPD).

[d] Parenthesis indicate credit taken.

TABLE 6-5. ANNUAL ENERGY REQUIREMENTS (TJ) FOR NO_x ABATEMENT SYSTEMS FOR A 270 Mg/d NITRIC ACID PLANT (Reference 6-6 and 6-26)[a]

	Basic Nitric Acid Plant	Catalyst Reduction	Molecular Sieve	Grande Paroisse	CDL/ Vitok	Masar	Goodpasture
Steam (Credit)	(75.2)	(136.18)	2.15	-	6.14	11.27	-
Electrical	--	11.56	29.08	8.13	23.94	1.80	1.38
Natural Gas	172.0	245.12	-	-	-	-	
Oil	-	-	17.20	-	-	-	-
	96.8	108.94	48.43	8.13	30.08	13.07	1.38

[a] This table is given in Appendix A in English units..

TABLE 6-6. BASIS FOR TABLES 6-4 AND 6-5 (Reference 6-6)[a]

(Plant Capacity 270 Mg/day and 926 Gg/yr)

(March 1975 Dollars, ENR Index = 2.126)

1. Operating Labor @ $6.1/hr
2. Maintenance Labor @ $7.0/hr
3. Overhead @ 100% of labor (including fringe benefits and supervision)
4. Cooling Water @ $0.008/1000 l
5. Boiler Feedwater @ $0.20/1000 l
6. Natural Gas @ $1.90/GJ
7. Oil @ $1.90/GJ
8. Depreciation @ 11 yr straight line
9. Return on Investment @ 20% of capital cost
10. Taxes and Insurance @ 2% of capital cost
11. Nitric Acid @ $ 99/Mg
12. Urea @ $176/Mg
13. Ammonium Nitrate @ $110/Mg
14. 1 kWh = 11.07 MJ
15. Electricity @ $0.02/kWh
16. Ammonia @ $173/Mg

[a] This table is given in Appendix A in English units.

Capital and operating costs for these processes are very low and are aided by credit for the byproducts (ammonium nitrate). In the Goodpasture process approximately 75 percent of the ammonia is reclaimed as ammonium nitrate.

Catalytic Reduction

The cost and energy data given in Tables 6-4 and 6-5 are for a natural gas fired nonselective catalytic reduction unit. The process is considerably more expensive than the other processes. Not only does a catalytic combustor have a high capital cost, but fuel costs are large (and will probably increase).

Costs for selective catalytic reduction are not included in Table 6-4. Capital costs are estimated as $100,000 to $125,000 for a 270 Mg per day unit by Gulf (Reference 6-27). Operating and maintenance costs are expected to be low except possibly for catalyst replacement. The major operating expense is the cost of ammonia for reaction with NO_x.

Molecular Sieve

Both capital and operating costs for the molecular sieve process are high. Fuel for the regeneration phase, high maintenance costs, and catalyst replacement are the primary contributors to the operating costs. Not included in the cost figures are any extra costs which may result from upsets or process alterations in the nitric acid plant as a result of the cyclic operation of the abatement unit.

6.2 NITRIC ACID USES

Important uses of nitric acid and the estimated quantities consumed in each are listed in Table 6-7. Approximately 65 percent of the nitric acid produced in the United States is consumed in making ammonium nitrate, of which approximately 80 percent is used for fertilizer manufacturing. Adipic acid manufacture, the second largest use, consumes only about 7 percent. Other uses include metal pickling and etching, nitrations and oxidations of organic compounds, and production of metallic nitrates.

6.2.1 Ammonium Nitrate Manufacture

6.2.1.1 Process Description

Ammonium nitrate is produced by the direct neutralization of nitric acids with ammonia:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \qquad (6\text{-}10)$$

TABLE 6-7. ANNUAL NITRIC ACID CONSUMPTION IN THE UNITED STATES, 1974 (Reference 6-3 and 6-6)

Product	Quantity of HNO_3 used in manufacture	
	Gg	10^3 tons
Ammonium Nitrate	4830	5324
Adipic Acid	520	573
Nitrobenzene	74	82
Potassium Nitrate	37	40
Miscellaneous Fertilizers	371	409
Military, other than NH_4NO_3	258	286
Isocynates	111	122
Steel Pickling	37	41
Other	1193	1315
Total Nitric Acid Production	7431	8192

About 735 kg (1600 lb) of nitric acid (100 percent equivalent) and 190 to 205 kg (420 to 450 lb) of anhydrous ammonia are required to make 909 kg (1 ton) of ammonium nitrate. In actual practice, 100 percent nitric acid is not used, and typical feed acid contains 55 to 60 percent HNO_3. The product is an aqueous solution of ammonium nitrate, which may be used as liquid fertilizer or converted into a solid product. The heat of reaction is usually used to evaporate part of the water, giving typically a solution of 83 to 86 percent ammonium nitrate. Further evaporation to a solid may be accomplished in a falling-film evaporator (Reference 6-28), in a disk-spraying plant (Reference 6-29), or by evaporation to dryness in a raked shallow open pan (graining). The graining process is no longer used due to hazardous conditions.

A majority of the solid ammonium nitrate produced in the United States is formed by "prilling", a process in which molten ammonium nitrate flows in droplets from the top of a tower countercurrent to a rising stream of air, which cools and solidifies the melt to produce pellets or prills (Reference 6-3).

6.2.1.2 Emissions

No significant amount of NO_x is produced in this process; the most likely source of nitric acid emissions would be the neutralizer. The vapor pressure of ammonia, however, is much higher than the vapor pressure of nitric acid, and the release of nitric acid fumes or NO_x is believed to be negligible (Reference 6-30), especially since a slight excess of NH_3 is used to reduce product decomposition.

6.2.2 Organic Oxidations

6.2.2.1 Process Description

Nitric acid is used as an oxidizing agent in the commercial preparation of adipic acid, terephthalic acid, and other organic compounds containing oxygen. The effective reagent is probably NO_2, which has very strong oxidizing power.

Adipic acid ($COOH \cdot (CH_2)_4 \cdot COOH$) is a di-basic acid used in the manufacture of synthetic fibers. It is an odorless white crystalline powder which is manufactured by the catalytic oxidation of cyclohexane, with cyclohexanone and cyclohexanol as intermediates. About 618 Gg (681,000 tons) of adipic acid were manufactured in 1975 (Reference 6-31). Approximately 90 percent of adipic acid is consumed in the manufacture of nylon 6/6.

In the United States, adipic acid is made in a two-step operation. The first step is the catalytic oxidation of cyclohexane by air to a mixture of cyclohexanol and cyclohexanone. In the second step, adipic acid is made by the catalytic oxidation of the cyclohexanol/cyclohexanone mixture using 45 to 55 percent nitric acid. The product is purified by crystallization (Reference 6-32). The whole operation is continuous. The chemistry of the reactions in the two steps is:

$$\text{cyclohexanone} + \text{nitric acid} \rightarrow \text{adipic acid} + NO_x + H_2O \qquad (6\text{-}11)$$

$$\text{cyclohexanol} + \text{nitric acid} \rightarrow \text{adipic acid} + NO_2 + H_2O \qquad (6\text{-}12)$$

The main nitrogen compounds formed in the above reactions are NO, NO_2, and N_2O. The dissolved oxides are stripped from the adipic acid/nitric acid solution with air and steam. The NO and NO_2 are recovered by absorption in nitric acid. The off-gas from the NO_x absorber is the major contributor to NO_x emissions from the adipic acid manufacturing process.

Nitric acid is used for the oxidation of other organic compounds in addition to the adipic acid, but none approaches the adipic acid product volume.

Terephthalic acid is an intermediate in the production of polyethylene terephthalate, which is used in polyester, films, and other miscellaneous products. Terephthalic acid can be produced in various ways, one of which is by the oxidation of paraxylene by nitric acid (Reference 6-33). In 1970, the process was used for about a third of terephthalic acid production and accounted for approximately 20 percent of NO_x emissions from nitration processes. Since 1975, however, the use of nitric acid as a feedstock in the production of terephthalic acid has been discontinued (Reference 6-34). No NO_x is now generated in terephthalic acid plants.

6.2.2.2 Emissions

The off-gases leaving the adipic acid reactor after nitric acid oxidation of organic materials may contain as much as 30 percent NO_x before processing for acid recovery (Reference 6-35). One of the principal compounds of the off gas, N_2O, is not counted as NO_x, since it is not oxidized to NO_x in the atmosphere and is considered harmless. The seven adipic acid manufacturing plants in the United States generated about 14.5 Gg (16,100 tons) of NO_x in 1975 (Reference 6-31) from a total acid production of 618 Gg (681,000 tons). This gives an average emission factor of 23.7 kg NO_2/Mg (47.4 lb NO_2/ton) compared to the nominal value 6 kg NO_2/Mg (12.0 lb NO_2/ton) specified by AP-42 (Reference 6-36).

6.2.2.3 Control Techniques

In commercial operations, economy requires the recovery of NO_x as nitric acid. It is recovered by mixing the off-gas with air and sending the stream to an absorbing tower, where nitric acid is recovered as the stream descends and unrecoverable N_2O and nitrogen pass off overhead.

If the resulting emission rates are too high, further reduction could be attempted by standard techniques such as extended absorption or wet chemical scrubbing. These techniques are described in Section 6.1.3. A potential, long-range control for eliminating NO_x from organic oxidation processing is the replacement of nitric acid as an oxidant by catalytic processes using air oxygen. The laboratory catalytic oxidation of cyclohexanol and cyclohexanone by air to adipic acid has also been reported, but no commercial process is known (Reference 6-37).

6.2.2.4 Costs

Economy requires that nitric acid be recovered from reactor off-gas in large-scale organic oxidations using nitric acid as the oxidizing agent. For example, the incentive for acid recovery for a 270 Mg/d (300 tons/day) adipic acid plant would be about $\$2.48 \times 10^6$ per year. This figure is based on recovering 0.3 kg of HNO_3 per kg of adipic acid at a nitric acid cost of \$8.6 per 100 kg (Reference 6-38). The optimum economic recovery level depends upon economic factors at each installation.

6.2.3 Organic Nitrations

6.2.3.1 Process Description

Nitration is the treating of organic compounds with nitric acid (or NO_2) to produce nitro compounds or nitrates. The following equations illustrate the two most common types of reaction:

$$RH + HONO_2 \rightarrow RNO_2 + H_2O \qquad (6\text{-}13)$$

$$ROH + HONO_2 \rightarrow RONO_2 + H_2O \qquad (6\text{-}14)$$

Examples of products of the first reaction (C-nitration) are compounds such as nitrobenzene, nitrotoluenes, and nitromethane. Nitroglycerin (or glycerin trinitrate) and nitrocellulose are examples of compounds produced by the second reaction (O-nitration).

Nitrating agents used commercially include nitric acid, mixed nitric and sulfuric acids (mixed acids), and NO_2. Mixed nitric and sulfuric acid is most frequently used. The sulfuric acid functions to promote formation of NO_2^+ ions and to absorb the water produced in the reaction.

Nitrations are carried out in either batch or continuous processes. The trend is toward continuous processes, since control is more easily maintained, equipment is smaller, system holdup is smaller, and hazards are reduced. A multiplicity of specialty products such as dyes and drugs, which are produced in small volumes, will continue, however, to be manufactured by small batch nitrations.

Batch nitration reactors are usually covered vessels provided with stirring facilities and cooling coils or jackets. The reactor bottom is sloped, and product is withdrawn from the lowest point. When products are potentially explosive, a large tank containing water (drowning tank) is provided so that the reactor contents can be discharged promptly and "drowned" in case of abnormal conditions.

When the reaction is completed, the reactor contents are transferred to a separator, where the product is separated from the spent acid. The product is washed, neutralized, and purified; spent acids are processed for recovery. Figure 6-12 illustrates a batch nitration process for manufacturing nitroglycerin (Reference 6-39).

Continuous nitration for nitroglycerin is carried out in many types of equipment. Two widely employed processes are the Schmid-Meissner process (illustrated in Figure 6-13) and the Biazzi process (illustrated in Figure 6-14). Both processes provide for continuous reaction, separation, water washing, neutralization, and purification. The Biazzi process makes greater use of impellers for contacting than the Schmid-Meissner, which uses compressed air to provide agitation during washing and neutralizing. Both types of equipment can be used for nitrating in general.

When mixed acid is used, the spent acid is recovered in a system similar to that shown in Figure 6-15. The mixed acid enters the top of the denitrating tower. Superheated steam is admitted at the bottom to drive off the spent nitric acid and NO_x overhead. The gases are passed through a condenser to liquefy nitric acid, which is withdrawn to storage; the uncondensed gases are then sent to an absorption tower. Weak sulfuric acid is withdrawn from the bottom of the denitrator tower and concentrated or disposed of by some convenient arrangement.

When nitric acid alone is used for nitration, the weak spent acid is normally recovered by sending it to an absorption tower, where it replaces some of the water normally fed as absorbent.

Nitrobenzene and dinitrotoluenes are produced in large volumes as chemical intermediates. Explosives such as TNT, nitroglycerin, and nitrocellulose are produced in significant but lesser volumes.

Nitrobenzene is manufactured in both continuous and batch nitration plants. Mixed acids containing 53 to 60 percent H_2SO_4, 32 to 39 percent HNO_3, and 8 percent water are used in batch operations, which may process 3.785 m^3 (1000 gallons) to 5.678 m^3 (1500 gallons) of benzene in 2 to 4 hours. Continuous plants, as typified by the Biazzi units (Figure 6-14) also use mixed acids.

The major use of nitrobenzene is in the manufacture of aniline. It is also used as a solvent. Nitrobenzene production in 1970 was an estimated 188 Gg (207,500 tons). Nitric acid requirements

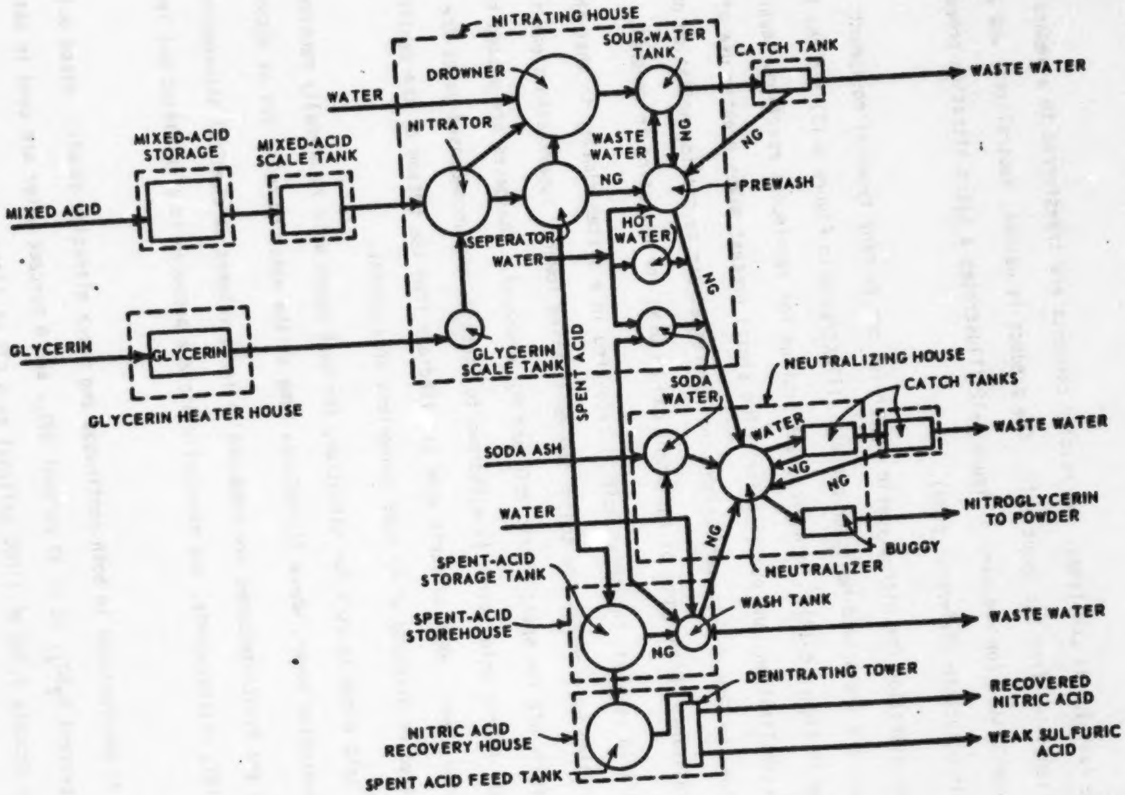

NITRATING HOUSE
MIXED-ACID STORAGE
MIXED-ACID SCALE TANK
MIXED ACID
WATER
DROWNER
NITRATOR
SOUR-WATER TANK
CATCH TANK
WASTE WATER
WASTE WATER
NG
NG
NG
PREWASH
SEPERATOR
WATER
HOT WATER
NG
GLYCERIN
GLYCERIN
GLYCERIN HEATER HOUSE
GLYCERIN SCALE TANK
SPENT ACID
SODA WATER
NEUTRALIZING HOUSE
CATCH TANKS
WASTE WATER
SODA ASH
WATER
NG
NG
NITROGLYCERIN TO POWDER
BUGGY
NEUTRALIZER
NG
WATER
SPENT-ACID STORAGE TANK
SPENT-ACID STOREHOUSE
WASH TANK
NG
WASTE WATER
DENITRATING TOWER
RECOVERED NITRIC ACID
NITRIC ACID RECOVERY HOUSE
WEAK SULFURIC ACID
SPENT ACID FEED TANK

Figure 6-12. Batch process for the manufacture of nitroglycerin (NG) (Reference 6-39).

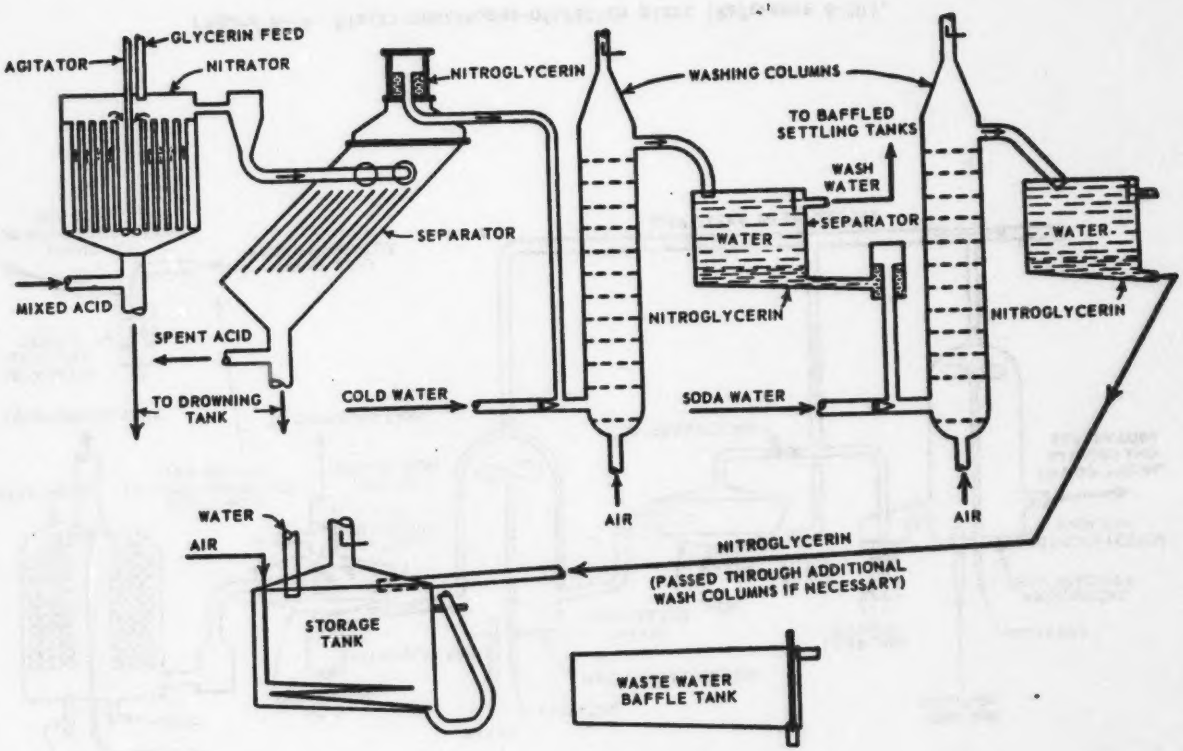

AGITATOR
GLYCERIN FEED
NITRATOR
NITROGLYCERIN
WASHING COLUMNS
TO BAFFLED SETTLING TANKS
WASH WATER
SEPARATOR
WATER
WATER
SEPARATOR
MIXED ACID
NITROGLYCERIN
NITROGLYCERIN
SPENT ACID
TO DROWNING TANK
COLD WATER
SODA WATER
AIR
AIR
WATER
AIR
NITROGLYCERIN
(PASSED THROUGH ADDITIONAL WASH COLUMNS IF NECESSARY)
STORAGE TANK
WASTE WATER BAFFLE TANK

Figure 6-13. Schmid-Meissner continuous-nitration plant (Reference 6-39).

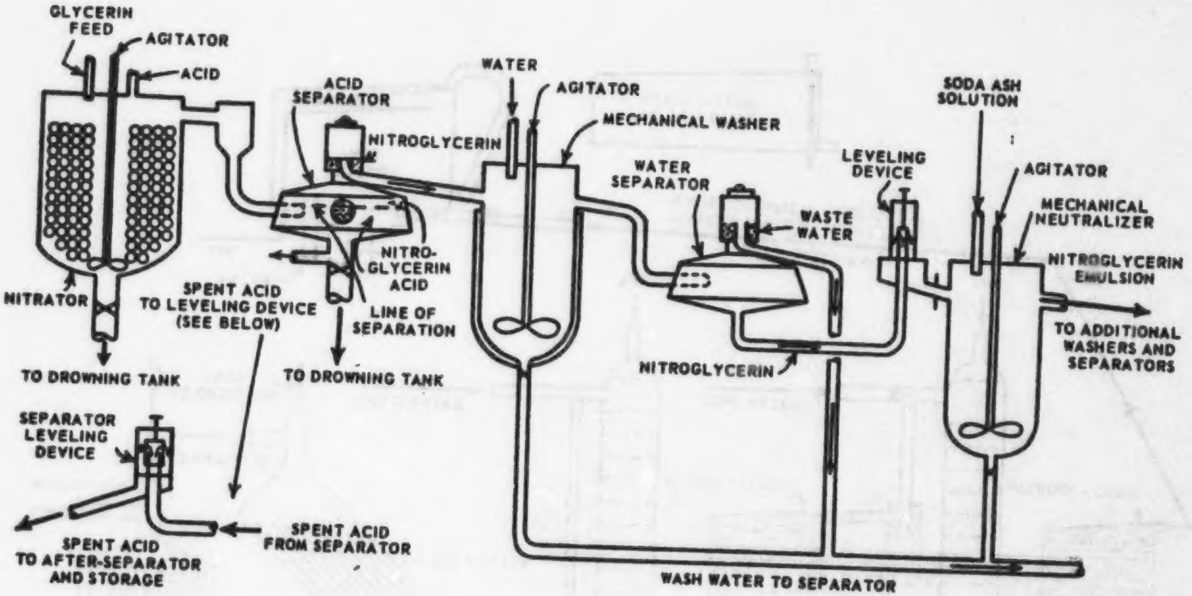

GLYCERIN FEED
AGITATOR
ACID
NITRATOR
TO DROWNING TANK
ACID SEPARATOR
NITROGLYCERIN
NITRO-GLYCERIN
ACID
LINE OF SEPARATION
SPENT ACID TO LEVELING DEVICE (SEE BELOW)
TO DROWNING TANK
SEPARATOR LEVELING DEVICE
SPENT ACID TO AFTER-SEPARATOR AND STORAGE
SPENT ACID FROM SEPARATOR
WATER
AGITATOR
MECHANICAL WASHER
WATER SEPARATOR
WASTE WATER
NITROGLYCERIN
LEVELING DEVICE
SODA ASH SOLUTION
AGITATOR
MECHANICAL NEUTRALIZER
NITROGLYCERIN EMULSION
TO ADDITIONAL WASHERS AND SEPARATORS
WASH WATER TO SEPARATOR

Figure 6-14. Biazzi continuous-nitration plant (Reference 6-39).

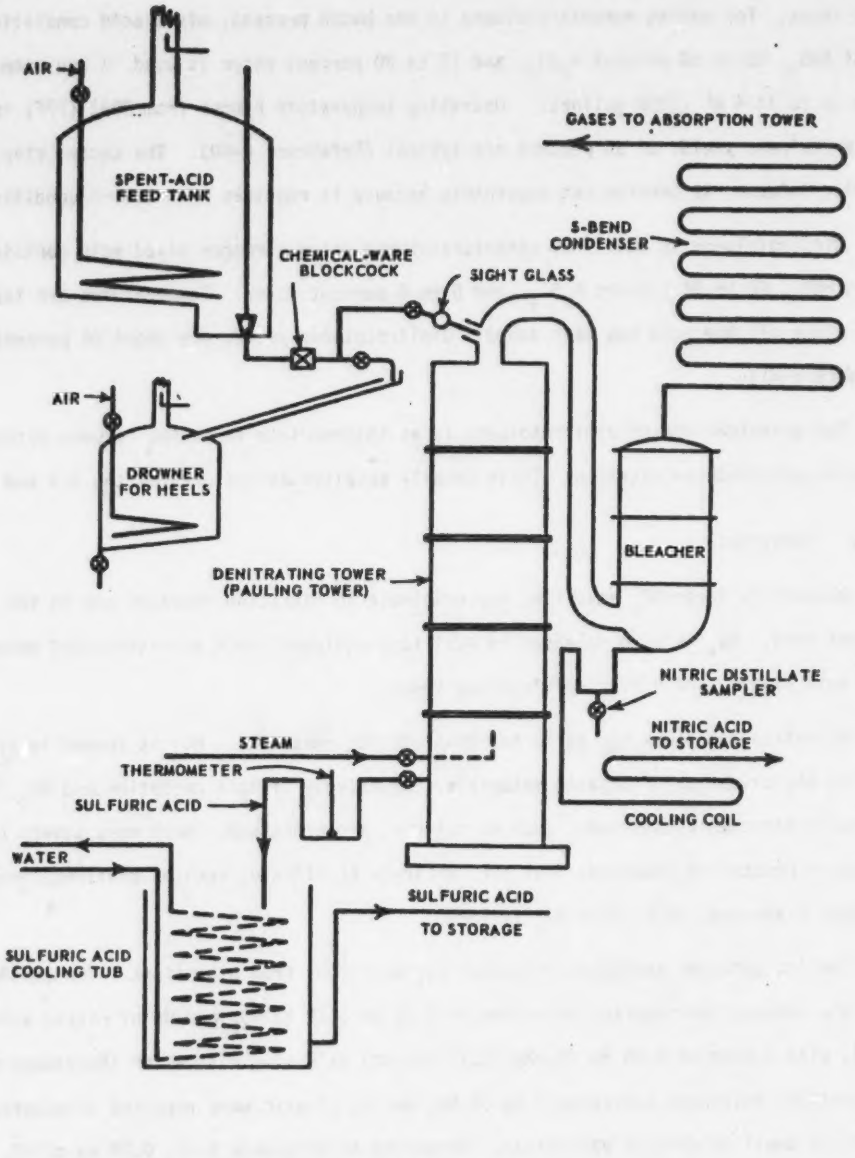

AIR
SPENT-ACID FEED TANK
GASES TO ABSORPTION TOWER
S-BEND CONDENSER
CHEMICAL-WARE BLOCKCOCK
SIGHT GLASS
AIR
DROWNER FOR HEELS
BLEACHER
DENITRATING TOWER (PAULING TOWER)
NITRIC DISTILLATE SAMPLER
STEAM
NITRIC ACID TO STORAGE
THERMOMETER
SULFURIC ACID
COOLING COIL
WATER
SULFURIC ACID TO STORAGE
SULFURIC ACID COOLING TUB

Figure 6-15. Recovery of spent acid (Reference 6-39).

are approximately 0.54 kg per kg of nitrobenzene (Reference 6-39). On this basis, nitric acid used in nitrobenzene synthesis was estimated at 126 Gg (139,000 tons) for 1970.

Dinitrotoluene is manufactured in two stages in both continuous and batch units. The first stage is the nitration of toluene to mononitrotoluene, which is nitrated to dinitrotoluene in the second stage. For making mononitrotoluene in the batch process, mixed acid consisting of 28 to 32 percent HNO_3, 52 to 56 percent H_2SO_4, and 12 to 20 percent water is used in equipment sized to handle up to 11.4 m^3 (3000 gallons). Operating temperature ranges from 298K (77F) to 313K (104F). Mononitrotoluene yields of 96 percent are typical (Reference 6-40). The second step, the production of dinitrotoluene, is carried out separately because it requires more severe conditions.

Dinitrotoluene is made from mononitrotoluene using stronger mixed acid containing 28 to 32 percent HNO_3, 60 to 64 percent H_2SO_4, and 5 to 8 percent water. Temperatures are increased to 363K (194F) after all the acid has been added. Dinitrotoluene yields are about 96 percent of theoretical (Reference 6-41).

The principal use of dinitrotoluene is as intermediate in making toluene diisocyanate (TDI) for use in polyurethane plastics. It is usually supplied as mixtures of the 2,4 and 2,6 isomers.

6.2.3.2 Emissions

Relatively large NO_x emissions may originate in nitration reactors and in the denitration of the spent acid. NO_x is also released in auxiliary equipment such as nitric acid concentrators, nitric acid plants, and nitric acid storage tanks.

Nitration reactions per se do not generate NO_x emissions. NO_x is formed in side reactions involving the oxidation of organic materials. Relatively little oxidation and NO_x formation occur when easily nitratable compounds, such as toluene, are processed. Much more severe conditions are required in processing compounds that are difficult to nitrate, such as dinitrotoluene; more oxidation takes place and, thus, more NO_x is formed.

Limtied data are available on actual NO_x emissions from nitrations. For continuous nitrations, one company has reported emissions of 0.06 to 0.12 kg NO_2 per Mg of nitric acid (0.12 to 0.24 lb/ton), with a mean of 0.09 kg NO_2/Mg (0.18 lb/ton) at a single location (Reference 6-40). At the same location, emissions averaging 7 kg of NO_2 per Mg of acid were reported in manufacturing specialty products in small batch-type operations. According to Reference 6-42, 0.25 kg of NO_2 per Mg of nitric acid (0.5 lb/ton) are generated in the production of nitrobenzene. In the manufacture of dinitrotoluence, 0.135 kg of NO_2 is estimated to be generated for every Mg of nitric acid used (0.27 lb/ton).

Using the Reference 6-42 emission factors as a lower limit, and 7 kg NO_x per Mg HNO_3 (14 lb/ton), (Reference 6-40) as upper limits for nitrations, the NO_x emissions in 1970 would have the range indicated in Table 6-8. Even using the upper limit, NO_x emissions from nitrobenzene and dinitrotoluene synthesis are relatively small but may present local nuisance problems. Since the upper limit represents specialty batch operations on a small scale, the emissions are probably much higher than would be encountered in large volume production of these products in either batch or continuous equipment.

6.2.3.3 Control Techniques

In large batch or continuous nitrations, operations are carried out in closed reactors. Fumes are conducted from the reactor, air is added, and the mixture enters an absorption tower for recovery of nitric acid. If too much NO_2 remains in the residual gas from the absorber, it may be further reduced by techniques such as wet chemical scrubbing. Details of the control techniques are discussed in Section 6.1.3.

Noncondensable gas from acid denitration is treated in the same manner as reactor gas. A common absorber is sometimes employed.

Small batch nitrators used in manufacturing specialties such as drugs and dyes are small-volume, high-intensity NO_x emitters. In one plant, reaction times ranged from 3 to 12 hours, depending on the product made. From 3 to 850 batches of each product were made each year. Emissions ranged from 0.7 to 130 kg of NO_x per Mg of nitric acid (0.14 to 260 lb/ton) with a median of 21 kg per Mg of nitric acid (21 lb/ton). The median emission was 7 kg per Mg (14 lb/ton) when one product was excluded from the calculations. The emissions, which are vented in individual stacks, are brown in color for a few hours per batch.

Caustic scrubbing and NO_x incineration are regarded as the most plausible controls for specialty batch nitrations. Catalytic reduction is usually ruled out because of organic and other impurities in the gas. Neither control is considered highly efficient in this application.

The intermittent character of emissions makes them difficult to control and contributes to very high pollution abatement costs per ton of nitric acid consumed. According to DuPont, operating costs for such equipment would render approximately half of the small batch nitrations so uneconomical that the manufacture of these products would be terminated (Reference 6-40). Large batches may be suitable for conversion to continuous operating, but small batches are not.

TABLE 6-8. ESTIMATED NO_x EMISSIONS FROM ORGANIC NITRATIONS IN 1970 (REFERENCE 6-42).

Product	1970 Production Mg (tons)	Estimated HNO_3 consumption Mg (tons)	NO_x Emissions Mg (tons)	
			Lower limit	Upper limit
Nitrobenzene	233,600 (257,000)	126,099 (139,000)	883 (973)	
Dinitrotoluene	131,542 (145,000)	101,151 (111,500)	708 (780)	

6.2.3.4 Costs

Fume incinerator investments are quoted at $10,000 to $20,000 by one source (Reference 6-43). Another suggests that investments of $75,000 to $150,000 are necessary for flame abatement facilities for existing small batch nitrators and $75,000 to $250,000 for existing large nitrators. Annual operating costs were estimated at $25,000 to $85,000 per product for small batch nitrators and $25,000 to $40,000 for continuous nitrators (Reference 6-40).

6.2.4 Explosives: Manufacture and Use

6.2.4.1 Process Description

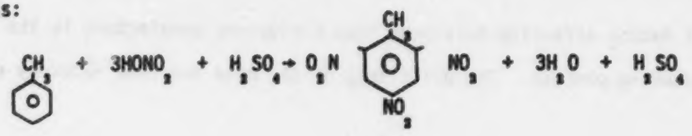
An explosive is a material that, under the influence of thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of large amounts of heat and gas. Explosives fall into two major categories: high (industrial) explosives and low explosives.

Industrial explosives in the United States consist of over 80 percent by weight of ammonium nitrate and some 10 percent of nitro organic compounds. During 1975, an estimated 1.4 Tg (3.1 x 10^9 pounds) of industrial explosives were manufactured, which is about 13 percent higher than the 1974 productions (Reference 6-44). High explosives are less sensitive to mechanical or thermal shock, but explode with great violence when set off by an initiating explosive (Reference 6-45). Low explosives, such as nitrocellulose, undergo relatively slow autocombustion when set off and evolve large volumes of gas in a definite and controllable manner.

Production and consumption data for military explosives are classified. Some of the more important ingredients in military explosives are known, however: trinitrotoluene (TNT), penterythritol tetranitrate (PETN), cyclotrimethylene-tri-nitramine (RDX), and trinitrophenylmethylnitramine (Tetryl). Nitration is an essential step in the manufacture of each of these.

PETN is most commonly used in conjunction with TNT in the form of pentolites, made by incorporating PETN into molten TNT. RDX is used in admixture with TNT, or compounded with mineral jelly to form a useful plastic explosive. Tetryl is most often used as a primer for other less sensitive explosives.

TNT (symmetrical trinitrotoluene) may be prepared by either a continuous process or a batch, three-stage nitration process using toluene, nitric acid, and sulfuric acid as raw materials. In the batch process, a mixture of oleum (fuming sulfuric acid) and nitric acid that has been concentrated to a 97 percent solution is used as the nitrating agent. The overall reaction may be expressed as:



(6-15)

Spent acid from the nitration vessels is fortified with makeup 60 percent nitric acid before entering the next nitrator. Fumes from the nitration vessels are collected and removed from the exhaust by an oxidation-absorption system. Spent acid from the primary nitrator is sent to the acid recovery system in which the sulfuric and nitric acid are separated. The nitric acid is recovered as a 60 percent solution, which is used for refortification of spent acid from the second and third nitrators. Sulfuric acid is concentrated in a drum concentrator by boiling water out of the dilute acid. The product from the third nitration vessel is sent to the wash house at which point asymmetrical isomers and incompletely nitrated compounds are removed by washing with a solution of sodium sulfite and sodium hydrogen sulfite (Sellite). The wash waste (commonly called red water) from the purification process is discharged directly as a liquid waste stream, is collected and sold, or is concentrated to a slurry and incinerated in rotary kilns. The purified TNT is solidified, granulated, and moved to the packing house for shipment or storage. A schematic diagram of TNT production by the batch process is shown in Figure 6-16.

Nitrocellulose is prepared by the batch-type "mechanical dipper" process. Cellulose, in the form of cotton linters, or specially prepared wood pulp, is purified, bleached, dried, and sent to a reactor (niter pot) containing a mixture of concentrated nitric acid and a dehydrating agent such as sulfuric acid, phosphoric acid, or magnesium nitrate. The overall reaction may be expressed as:

$$C_6H_7O_2(OH)_3 + 3HONO_2 + H_2SO_4 \rightarrow C_6H_7O_2(ONO_2)_3 + 3\ H_2O + H_2SO_4 \qquad (6\text{-}16)$$

When nitration is complete, the reaction mixtures are centrifuged to remove most of the spent acid. The spent acid is fortified and reused or otherwise disposed. The centrifuged nitrocellulose undergoes a series of water washings and boiling treatments for purification of the final product.

6.2.4.2 Emissions

The major emissions from the manufacture of explosives are nitrogen oxides and nitric acid mists. Emissions of nitrated organic compounds may also occur from many of the TNT process units. In the manufacture of TNT, vents from the fume recovery system, and nitric acid concentrators are the principal sources of emissions. Emissions may also result from the production of Sellite solution and the incineration of "red water". Many plants now sell the red water to the paper industry where it is of economic importance.

Principal sources of emissions from nitrocellulose manufacture are from the reactor pots and centrifuges, spent acid concentrators, and boiling tubs used for purification.

The most important factor affecting emissions from explosives manufacture is the type and efficiency of the manufacturing process. The efficiency of the acid and fume recovery systems for

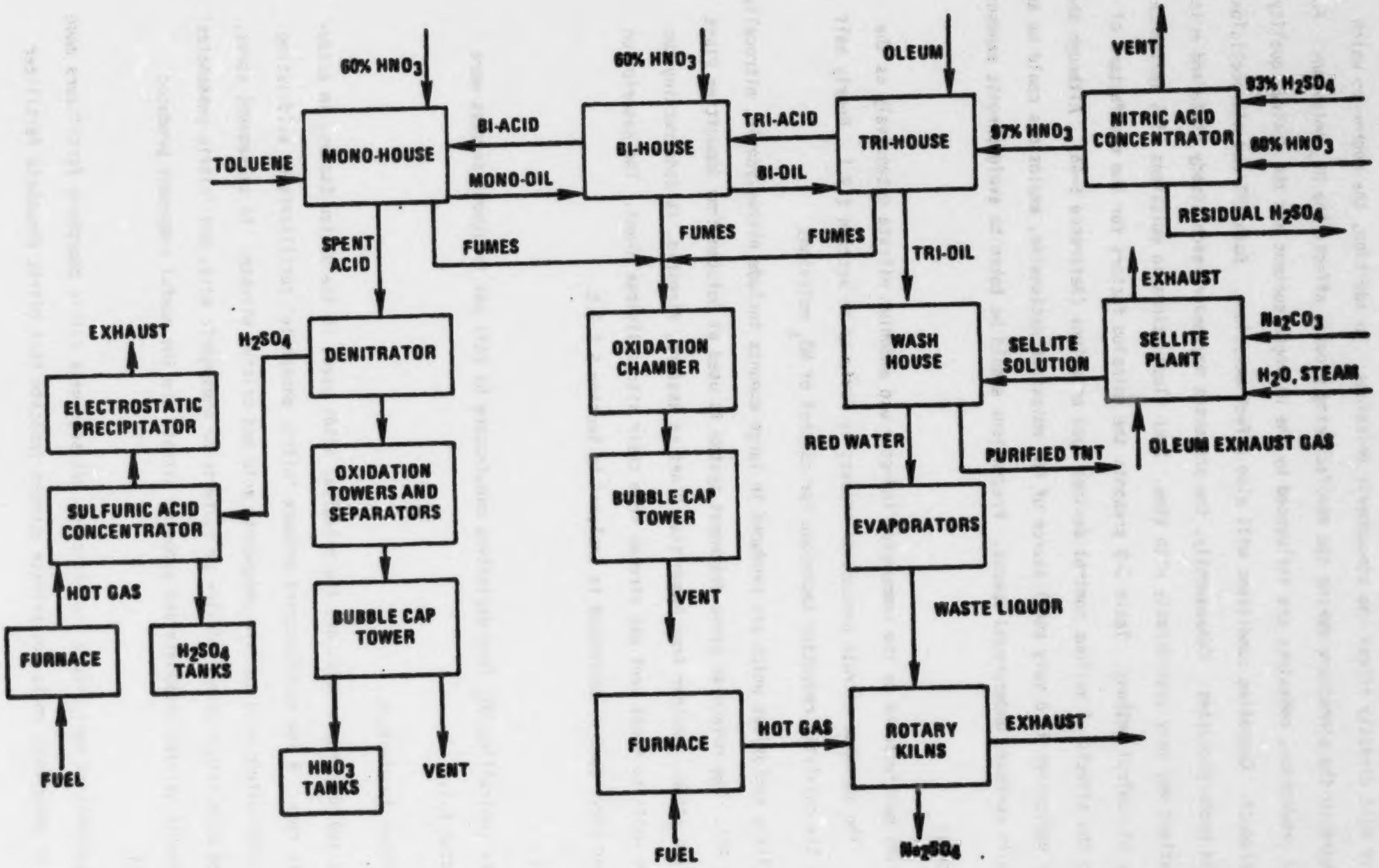

60% HNO3
60% HNO3
OLEUM
VENT
93% H2SO4
80% HNO3
TOLUENE
MONO-HOUSE
BI-ACID
MONO-OIL
BI-HOUSE
TRI-ACID
BI-OIL
TRI-HOUSE
97% HNO3
NITRIC ACID CONCENTRATOR
RESIDUAL H2SO4
SPENT ACID
FUMES
FUMES
FUMES
TRI-OIL
EXHAUST
SELLITE PLANT
Na2CO3
H2O, STEAM
OLEUM EXHAUST GAS
SELLITE SOLUTION
WASH HOUSE
RED WATER
PURIFIED TNT
EXHAUST
H2SO4
DENITRATOR
OXIDATION CHAMBER
ELECTROSTATIC PRECIPITATOR
OXIDATION TOWERS AND SEPARATORS
BUBBLE CAP TOWER
EVAPORATORS
SULFURIC ACID CONCENTRATOR
HOT GAS
VENT
WASTE LIQUOR
BUBBLE CAP TOWER
FURNACE
H2SO4 TANKS
FURNACE
HOT GAS
ROTARY KILNS
EXHAUST
HNO3 TANKS
VENT
FUEL
FUEL
Na2SO4

Figure 6-16. Trinitrotoluene (batch process) manufacturing diagram (Reference 6-45).

TNT manufacture will directly affect the atmospheric emissions. In addition, the degree to which acids are exposed to the atmosphere during the manufacturing process affects the NO_x emissions. For nitrocellulose production, emissions are influenced by the nitrogen content and the desired quality of the final product. Operating conditions will also affect emissions. Both TNT and nitrocellulose are produced in batch processes. Consequently, the processes may never reach steady state and emission concentrations may vary considerably with time. Such fluctuations in emissions will influence the efficiency of control methods. Table 6-9 presents the emission factors for the manufacture of explosives and the effects of various control devices upon emissions (Reference 6-45). Although the manufacture of explosives is a very small source of NO_x emissions nationwide, explosions could be an intense source in confined underground spaces. Precautions should be taken to avoid chronic exposure.

6.2.4.3 Controls

Explosives manufactured by the commercial industry use ammonium nitrate extensively as the base material. The ammonium nitrate production process is reviewed in Section 6.2.1. Nearly half the plants use the catalytic reduction technique for control of NO_x emissions.

The military explosives which are produced in large amounts include nitroglycerin, nitrocellulose, TNT, and RDX. The molecular sieve abatement system is used at Holston Army Ammunition Plant in Kingsport, Tennessee. Another Army Ammunition Plant at Radford, Virginia, is constructing two molecular sieve units to treat vent gas streams from their nitrocellulose plant. The description of the molecular sieve control technique is included in Section 6.1.3.5.

6.2.4.4 Costs

Costs for controlling NO_x from explosives manufacture by tail gas treatment process were covered in Section 6.1.4.

6.2.5 Fertilizer Manufacture

Sulfuric and phosphoric acids are the principal acids used, in the United States, in acidulating phosphate rock. A few manufacturers produce "nitric phosphate" fertilizers by acidulating phosphate rock with nitric acid to form phosphoric acid and calcium nitrate. In subsequent steps, ammonia is added with either carbon dioxide or sulfuric or phosphoric acid, and "nitric phosphates" are formed. Dibasic calcium phosphate and ammonium nitrate are the useful compounds produced (Reference 6-48).

U.S. Department of Agriculture statistics do not segregate nitric phosphate fertilizers made by acidulation of phosphoric rock; but private sources indicate that nitric phosphate fertilizer

TABLE 6-9. EMISSION FACTORS FOR MANUFACTURE OF EXPLOSIVES (REFERENCE 6-45)

Type of process	Nitrogen oxides[a] (NO_2)	
	kg/Mg	lb/ton
TNT — batch process[b]		
Nitration reactors		
Fume recovery	12.5(3-19)	25(6-38)
Acid recovery	27.5(0.5-68)	55(1-136)
Nitric acid concentrators	18.5(8-36)	37(16-72)
Red water incinerator		
Uncontrolled[c]	13(0.75-50)	26(1.5-101)
Wet scrubber[d]	2.5	5
Sellite exhaust	—	—
TNT — continuous process[e]		
Nitration reactors		
Fume recovery	4(3.35-5)	8(6.7-10)
Acid recovery	1.5(0.5-2.25)	3(1-4.5)
Red water incinerator	3.5(3-4.2)	7(6.1-8.4)
Nitrocellulose[e]		
Nitration reactors[f]	7(1.85-17)	14(3.7-34)
Nitric acid concentrator	7(5-9)	14(10-18)

[a] For some processes considerable variations in emissions have been reported. The average of the values reported is shown first, with the ranges given in parentheses. Where only one number is given, only one source test was available.

[b] Reference 6-46

[c] Use low end of range for modern, efficient units and high end of range for older, less efficient units.

[d] Apparent reductions in NO_x and particulate after control may not be significant because these values are based on only one test result.

[e] Reference 6-47

[f] For product with low nitrogen content (12 percent), use high end of range. For products with higher nitrogen content, use lower end of range.

made in this manner was estimated at 450 Gg (500,000 tons) in 1967, and nitric acid consumptions at 135 Gg (150,000 tons) (Reference 6-49).

NO_x emissions are dependent on the quantity of carbonaceous material in the rock, since NO_x is formed as nitric acid oxidizes the carbonaceous matter. The use of calcined rock avoids the production of NO_x.

Air pollution abatement by fertilizer manufacturers' efforts has centered on reducing particulates and fluorides emissions, which are severe problems. The water scrubbing used to reduce these pollutants would be expected to reduce NO_x emissions to only a minor degree. Although no measurements of NO_x emissions are available, brown plumes are said to occur.

One company has found that the addition of urea to the acidulation mixture reduces NO_x emissions and eliminates the brown plume (Reference 6-49). Urea, as discussed in Section 6.1.3.3 reacts with nitric and nitrous acids to form N_2.

6.2.6 Metals Pickling

The principal use of nitric acid in metals pickling is in treating stainless steel. Mill scales on stainless steels are hard and are difficult to remove. Pickling procedures vary; sometimes a 10 percent sulfuric acid bath at 333K (140F) to 344K (160F) is followed by a bath at 328K (130F) to 339K (150F) with 10 percent nitric acid and 4 percent hydrofluoric acid. The first bath loosens the scale, and the second removes it. A continuous system for stainless steel strip consists of two tanks containing 15 percent hydrochloric acid, followed by a tank containing 4 percent hydrofluoric and 10 percent nitric acid at 339K (150F) to 350K (170F). One effective method is the use of molten salts of sodium hydroxide to which is added some agent such as sodium hydride. This may be followed by a dilute nitric acid wash (Reference 6-50).

No measurements were found of emission rates from nitric acid pickling of stainless steel. Treating equipment should be properly hooded and ventilated and the fumes scrubbed to protect workers. Urea would probably control the NO_x emissions.

Nitric acid is also used in the chemical milling of copper or iron from metals that are not chemically attacked by nitric acid, and for bright-dipping copper. In the latter operation, a cold solution of nitric and sulfuric acid has been customarily used. It has been reported that copper can be bright-dipped on cold nitric acid alone when urea is added. A highly acceptable finish is obtained, and NO_x fumes are eliminated.

Sulfuric acid should not be used with the nitric acid-urea mixture since nitrourea, an explosive, can form. Not more than 62 ml of urea per liter should be added, and satisfactory operation can be obtained with only 15 ml per liter.

In chemical milling, the addition of 46 to 62 ml of urea per liter of 40 percent nitric acid will reduce NO_2 emissions from 8,000 ppm to levels below 10 ppm, provided a bubble disperser is used (Reference 6-51).

A small, but intense, source of NO_x occurs in the manufacture of tungsten filaments for lightbulbs. Tungsten filaments are wound on molybdenum cores, and after heat-treating, the cores are dissolved in nitric acid.

Reference 6-43 describes air pollution equipment for reducing the dense NO_2 fumes given off periodically when trays of the filaments are dissolved. The fumes pass over a charcoal adsorber bed, which adsorbs NO_x as fumes are generated and desorbs when no fumes are being generated. This smooths out peaks and valleys in NO_x content in off-gases, which are then heated and combined with carbon monoxide and hydrogen from a rich combustion flame. The mixture is then passed through a bed of noble metal catalyst. A colorless gas is released from the equipment.

REFERENCES FOR SECTION 6

6-1 Manney, E.H. and S. Skopp, "Potential Control of Nitrogen Oxide Emissions from Stationary Sources," Presented at 62nd Annual Meeting of the Air Pollution Control Association, New York. June 22-26, 1969.

6-2 Freithe, W. and M. W. Packbier, "Nitric Acid: Recent Developments in the Energy and Environmental Area," presented at AICHE Symposium, Denver, Colorado, August 28, 1977.

6-3 Lowenheim, F.A. and M.K. Morgan, ed., Faith, Keyes, and Clark's Industrial Chemicals, 4th edition. New York, Wiley Interscience Publication, 1975.

6-4 "Strong Nitric Acid Process Features Low Utility Cost," Chemical Engineering, December 8, 1975, p. 98-99.

6-5 Personal communication. Mr. Dave Kirkbe, Davy Powergas, Houston, Texas, November 1977.

6-6 "Environmental Considerations of Selected Energy Conserving Manufacturing Process Options, Volume XV, Fertilizer Industry Report," EPA-600/7-76-0340, December 1976.

6-7 "Compilation of Air Pollution Emission Factors (Second Edition)," Publication No. AP-42, Environmental Protection Agency, Research Triangle Park, North Carolina, April 1973.

6-8 Gerstle, R.W. and R.F. Peterson, "Atmospheric Emissions from Nitric Acid Manufacturing Processes," National Center for Air Pollution Control, Cincinnati, Ohio, PHS Publication Number 999-AP-27, 1966.

6-9 Mayland, B.J., "Application of the CDL/VITOK Nitrogen Oxide Abatement Process," Presented to Sulfur and Nitrogen Symposium, Salford, Lancashire, U.K. April 1976.

6-10 Barber, J.C. and N.L. Faucett, "Control of Nitrogen Oxide Emissions from Nitric Acid Plants," Third Annual Air Pollution Control Conference, March 1973.

6-11 "NO_x Abatement in Nitric Acid and Nitric Phosphate Plants," Nitrogen, No. 93, Jan/Feb 1975.

6-12 "MASAR Process for Recovery of Nitrogen Oxides," Company brochure, MASAR, Inc.

6-13 Personal communication, Mr. Feaser, Plant manager, Illinois Nitrogen Plant, Marseilles, Ill. November 1977.

6-14 Service, W.J., R.T. Schneider, and D. Ethington, "The Goodpasture Process for Chemical Abatement and Recovery of NO_x," Conference on Gaseous Sulfur and Nitrogen Compound Emissions, Salford, England, April 1976.

6-15 Streight, H.R.L., "Reduction of Oxides of Nitrogen in Vent Gases," Chem. Eng., Vol. 36, 1958.

6-16 Gillespie, G.R., A.A. Boyum, and M.F. Collins, "Nitric Acid: Catalytic Purification of Tail Gas," Chemical Engineering Progress, Vol. 68, 1972.

6-17 Decker, L, "Incineration Technique for Controlling Nitrogen Oxides Emissions," Presented at the 60th Annual Meeting of the Air Pollution Control Association, Cleveland, Ohio, June 1967.

6-18 Andersen, H.C., W.J. Green, and D.R. Steele, "Catalytic Treatment of Nitric Acid Tail Gas," Ind. Eng. Chem., 53:199-204, March 1961.

6-19 Anderson, G.C. and W.J. Green, "Method of Purifying Gases Containing Oxygen and Oxides of Nitrogen (Englehard Industries, Inc., U.S. Patent No. 2, 970, 034), Official Gazette U.S. Patent Office, 762(5):969, January 31, 1961.

6-20 Newman, D.J. and L.A. Klein, "Apparatus for Exothermic Catalytic Reactions," (Chemical Construction Corp., U.S. Patent No. 3, 443, 910), Official Gazette U.S. Patent Office, 862 (2):514, May 1969.

6-21 Andersen, H.C., P.L. Romeo, and W.J. Green, "New Family of Catalysts for Nitric Acid Tail Gases," Nitrogen 50:33-36, November-December 1967.

6-22 Rosenberg, H.S., "Molecular Sieve NO_x Control Process in Nitric Acid Plants," Environmental Protection Technology Series, EPA-600/2-76-015, January 1976.

6-23 Chehaske, J.I. and J.S. Greenberg, "Molecular Sieve Tests for Control of NO_x Emissions from a Nitric Acid Plant," Volume 1, EPA-600/2-76-048a, March 1971.

6-24 Rosenburg, H.S., "Molecular Sieve NO_x Control Process in Nitric Acid Plants," EPA-600/2-76-015, January 1976.

6-25 Mayland, B.J. , The CDL/VITOK Nitrogen Oxides Abatement Process," Chenoweth Development Laboratory, Louisville, Ky.

6-26 Personal communication, Mr. Don Ethington, Goodpasture, Inc., Brownfield, Texas, November 1977, and February, 1978, and D. F. Carey, EPA-IERL, February 1978.

6-27 "New Unit for Nitric Plants Knocks Out NO_x," Chemical Week, July 28, 1976.

6-28 "Ammonium Nitrate," Hydrocarbon Process. 46:149, November 1967.

6-29 Miles, F.D., Nitric Acid -- Manufacture and Uses, London, Oxford University Press, 1961.

6-30 Private communication with Esso Research and Engineering Co.

6-31 Durocher, D.F., P.D. Spawn, and R.C. Galkiewicz, "Screening Study to Determine Need for Standards of Performance for New Adipic Acid Plants," draft report GCA-TR-76-16-G GCA Corporation, Bedford, Massachusetts, June 1976.

6-32 Goldbeck, M., Jr., and F.C. Johnson, "Process for Separating Adipic Acid Precursors," (E.I. DuPont de Nemours and Co., U.S. Patent No. 2, 703, 331). Official Gazette U.S. Patent Office. 692(1):110, March 1, 1955.

6-33 Burrows, L.A., R.M. Cavanaugh, and W.M. Nagle, "Oxidation Process for Preparations of Terephthalic Acid," (E.I. DuPont de Nemours and Co., U.S. Patent No. 2, 636, 99). Official Gazette U.S. Patent Office. 669(4):1209, April 28, 1953.

6-34 Durocher, D.F. *et al.*, "Screening Study to Determine Needs for Standards of Performance for New Sources of Dimethyl Terephthalate and Terephthalic Acid Manufacturing" Draft Final Report, GCA-TR-76-17-G. Submitted to EPA/OAQPS by GCA Corp., Bedford, Massachusetts, June 1976.

6-35 Lindsay, A.F., "Nitric Acid Oxidation Design in the Manufacture of Adipic Acid from Cyclohexanol and Cyclohexanone," Special Suppl. to Chem. Eng. Sci. 3:78-93, 1954.

6-36 Compilation of Air Pollutant Emission Factors, Environmental Protection Agency, AP-42, February 1972.

6-37 "Process for Oxidation of Cyclohexane and for the Production of Adipic Acid (British Patent No. 956, 779) and Production of Adipic Acid," (British Patent No. 956, 780). Great Britain Office. J. No. 3918:814, March 19, 1964.

6-38 Oil, Paint, and Drug Reptr. 195(6):1-48, April 21, 1969.

6-39 Crater, W. deC. Nitration. In: *Kirk-Othmer Encyclopedia of Chemical Technology*, Standen, A. (ed.). Vol. 9. New York, Interscience Publishers, 1952.

6-40 Private communication with E.I. DuPont de Nemours and Co., March 1969.

6-41 Urbanski, T., "Chemistry and Technology of Explosives," Jeczalikowa, I. and S. Laverton, (Trs.). Vol. I. New York, MacMillan Co., 1964.

6-42 Processes Research, Inc., "Air Pollution from Nitration Processes," Cincinnati, Ohio. APTD-1071, 1972.

6-43 Decker, L., "Incineration Technique for Controlling Nitrogen Oxides Emissions," Presented at the 60th Annual Meeting of the Air Pollution Control Association, Cleveland. June 11-16, 1967.

6-44 Nelson, T.P., and Pyle, R.E., "Screening Study to Determine the Need for New Source Performance Standards in the Explosives Manufacturing Industry," Draft Report, Radian Corporation, Austin, Texas, July 1976.

6-45 EPA, Compilation of Air Pollutant Emission Factors, AP-42, Supplement No. 5, December 1975.

6-46 Air Pollution Engineering Source Sampling Surveys, Radford Army Ammunition Plant. U.S. Army Environment Hygiene Agency, Edgewood Arsenal, Md.

6-47 Air Pollution Engineering Source Sampling Surveys, Volunteer Army Ammunition Plant and Joliet Army Ammunition Plant. U.S. Army Environmental Hygiene Agency, Edgewood Arsenal, Md.

6-48 McVickar, M.H. *et al.*, "Fertilizer Technology and Usage," Madison, Wisconsin, Soil Science Society of America, 1963.

6-49 Consumption of Commercial Fertilizers, U.S. Dept. of Agriculture. Statistical Reporting Service.

6-50 McGannon, H.E., *The Making, Shaping and Treating of Steel*, 8th ed. Pittsburgh, United States Steel Co., 1964.

6-51 Kerns, B.A., "Chemical Suppression of Nitrogen Oxides," Ind. Eng. Chem. Process Design Develop. Vol. 4, pp. 263-265, 1965.

APPENDIX A

SELECTED TABLES IN ENGLISH UNITS

This appendix contains the English engineering unit version of most of the large tables presented in the text. The tables are arranged sequentially in the order in which they appear in the text and have the same table number except for the prefix "A".

TABLE A2-2. EMISSIONS, EMISSION FACTORS, AND FUEL USAGE FOR STEAM GENERATION, 1974 — UTILITY BOILERS

Equipment Type	Firing Type	Fuel	Fuel Type	Fuel Usage 10^{12} Btu	Emission Factors lb $NO_2/10^6$ Btu	Total NO_x Emissions 10^6 tons NO_2
Field-Erected Watertube Boilers	Tangential Firing	Coal	Bituminous	4140.66	0.64	1.325
			Lignite	41.72	0.64	0.013
		Oil	Distillate	45.23	0.357	0.008
			Residual	1086.57	0.357	0.194
		Gas	—	867.55	0.30	0.130
	Horizontally Opposed Wall Firing	Coal, Dry Bottom	Bituminous	1229.22	0.75	0.461
			Lignite	11.97	0.88	0.005
		Coal, Wet Bottom	Bituminous	548.06	1.25	0.343
			Lignite	16.12	0.88	0.007
		Oil	Distillate	33.08	0.75	0.012
			Residual	792.40	0.75	0.297
		Gas	—	1378.23	0.70	0.482
	Front Wall Firing	Coal, Dry Bottom	Bituminous	1229.22	0.75	0.461
			Lignite	11.97	0.88	0.005
		Coal, Wet Bottom	Bituminous	540.23	1.25	0.338
			Lignite	14.32	0.88	0.006
		Oil	Distillate	33.08	0.75	0.012
			Residual	792.40	0.75	0.297
		Gas	—	954.22	0.70	0.334
	Vertical Firing	Coal, Dry Bottom	Anthracite	29.86	0.75	0.011
			Bituminous	378.83	0.75	0.142
			Lignite	2.99	0.75	0.001
	Cyclone	Coal, Wet Bottom	Bituminous	1020.62	1.30	0.663
			Lignite	12.64	0.88	0.006
		Oil	Distillate	2.92	0.75	0.001
			Residual	55.53	0.75	0.021
Field-Erected Watertube Boiler Stoker	Spreader	Coal	—	131.98	0.57	0.038
	Underfeed	Coal	—	56.60	0.57	0.016

TABLE A2-3. ANNUAL NO_x EMISSIONS AND FUEL CONSUMPTION COMPARISON FOR UTILITY BOILERS, 1974

Firing Type	NO_x Emission, 10^6 TPY[a] (column percent)				Fuel consumption, 10^{12} Btu (column percent)			
	Gas	Oil	Coal	Total	Gas	Oil	Coal	Total
Tangential	0.130(13.7)	0.202(24.0)	1.338(34.8)	1.67 (29.7)	868(27.1)	1132 (39.8)	4182(44.4)	6182 (40)
Horizontal front-wall	0.334(35.3)	0.309(36.7)	0.810(21.1)	1.453(25.8)	954(29.8)	825.5(29.1)	1796(19.1)	3575.5(23)
Opposed-wall	0.482(51)	0.309(36.7)	0.816(21.3)	1.607(28.6)	1378(43.1)	825.5(29.1)	1805(19.2)	4008.5(26)
Cyclone	–	0.022(2.6)	0.669(17.4)	0.691(12.3)	–	59 (2.1)	1033(11.0)	1092 (7)
Vertical	–	–	0.153(4.0)	0.153(2.7)	–	–	412(4.4)	412 (3)
Stokers	–	–	0.054(1.4)	0.054(1.0)	–	–	189(2.0)	189 (1)
Total	0.946(100)	0.842(100)	3.840(100)	5.628(100)	3200(100)	2842(100)	9417(100)	15459(100)

TABLE A2-4. ANNUAL FUEL USAGE FOR UTILITY BOILERS (10^{12} Btu)

Fuel	Source					
	Battelle 1971 (Reference 2-13)	MSST 1972 (Reference 2-4)	GCA 1974 (Reference 2-15)	Current 1974	Aerospace 1975, projected (Reference 2-17)	NEDS 1976[a]
Coal	5509	8424	8502	9417	9342	10369
Oil	2204	2593	3039	2842	2549	3665
Gas	3809	3765	3257	3200	2993	4447
Total	11522	14782	14798	15459	14884	18481

[a] Output of National Emissions Data System by Source Classification Code on August 16, 1976; contains data from 1974 and 1975.

TABLE A2-5. ANNUAL NO_X EMISSIONS FOR UTILITY BOILERS (10^6 tons)

Fuel	Source					
	Battelle 1971 (Reference 2-18)	MSST 1972 (Reference 2-4)	GCA 1974 (Reference 2-15)	Current 1974	Aerospace 1975, projected (Reference 2-17)	NEDS 1976[a]
Coal	2.214	3.788	4.700	3.840	4.897	4.55
Oil	0.773	0.768	0.810	0.842	0.667	1.29
Gas	1.144	1.114	0.960	0.946	0.673	1.05
Total	4.13	5.67	6.47	5.628	6.237	6.89

[a] Output of National Emissions Data System by Source Classification Code on August 16, 1976; contains data from 1974 and 1975.

TABLE A2-6. EMISSIONS, EMISSION FACTORS, AND FUEL USAGE FOR STEAM GENERATION, 1974 — INDUSTRIAL BOILERS

Equipment Type	Firing Type	Fuel	Fuel Type	Fuel Usage 10^{12} Btu	Emission Factors lb $NO_2/10^6$ Btu	Total NO_x Emissions 10^6 tons NO_2
Field-Erected Watertube Boilers >100 x 10^6 Btu/hr	Tangential Firing	Coal	—	141.32	0.640	0.045
		Oil	Residual	427.56	0.357	0.076
		Gas	Natural	391.47	0.301	0.059
			Process	54.99	0.230	0.006
	Horizontally Opposed-Wall Firing	Coal, Dry Bottom	—	42.40	0.750	0.016
		Coal, Wet Bottom	—	8.48	1.250	0.005
		Oil	Residual	414.67	0.573	0.119
		Gas	Natural	462.61	0.301	0.070
			Process	123.74	0.230	0.014
	Front-Wall Firing	Coal, Dry Bottom	—	42.40	0.750	0.016
		Coal, Wet Bottom	—	8.48	1.250	0.005
		Oil	Residual	414.67	0.573	0.119
		Gas	Natural	313.64	0.301	0.047
			Process	95.92	0.230	0.011
	Vertical Firing	Coal, Dry Bottom	—	9.36	0.750	0.004
	Cyclone	Coal, Wet Bottom	—	61.83	1.660	0.051
		Oil	Residual	35.21	0.573	0.010
Field-Erected Watertube Boilers 10-100 x 10^6 Btu/hr	Wall Firing	Oil	Distillate	58.61	0.150	0.004
			Residual	292.77	0.429	0.063
		Gas	Natural	806.41	0.230	0.093
			Process	37.14	0.230	0.004
Field-Erected Watertube Boilers Stokers	Spreader	Coal	—	768.80	0.417	0.160
	Underfeed	Coal	—	435.28	0.417	0.091
	Overfeed	Coal	—	209.16	0.625	0.065
	General, Not Classified	Coal	—	101.75	0.417	0.021

TABLE A2-6. ANNUAL FUEL CONSUMPTION FOR INDUSTRIAL BOILERS (10^{12} Btu) (Concluded)

Equipment Type	Firing Type	Fuel	Fuel Type	Fuel Usage 10^{12} Btu	Emission Factors lb $NO_2/10^6$ Btu	Total NO_x Emissions 10^6 tons NO_2
Packaged Watertube Bent Tube Straight Tube (Obsolete)	Wall Firing	Coal	–	42.40	0.750	0.016
		Oil	Distillate	146.81	0.157	0.012
			Residual	788.44	0.429	0.169
		Gas	Natural	2535.75	0.230	0.292
			Process	132.43	0.230	0.015
Packaged Watertube Stoker	Spreader	Coal	–	363.91	0.417	0.076
	Underfeed	Coal	–	567.60	0.417	0.118
	Overfeed	Coal	–	90.45	0.625	0.028
	General, Not Classified	Coal	–	59.36	0.417	0.012
Packaged Firetube Scotch	Wall Firing	Oil	Distillate	146.81	0.157	0.012
			Residual	735.15	0.429	0.158
		Gas	Natural	802.60	0.230	0.092
			Process	18.96	0.230	0.002
Packaged Firetube Firebox	Wall Firing	Oil	Distillate	56.45	0.157	0.004
			Residual	290.32	0.429	0.062
		Gas	Natural	693.23	0.230	0.080
			Process	18.96	0.230	0.002
Packaged Firetube Firebox Stoker	Spreader	Coal	–	16.96	0.417	0.004
	Underfeed	Coal	–	84.80	0.417	0.018
	Overfeed	Coal	–	11.31	0.625	0.004
Packaged Firetube HRT	Wall Firing	Oil	Distillate	28.23	0.157	0.002
			Residual	152.79	0.429	0.033
		Gas	–	364.82	0.230	0.042
Packaged Firetube HRT Stoker	Spreader	Coal	–	8.48	0.417	0.002
	Underfeed	Coal	–	42.40	0.417	0.009
	Overfeed	Coal	–	5.65	0.625	0.002

TABLE A2-7. ANNUAL FUEL CONSUMPTION FOR INDUSTRIAL BOILERS (10^{12} Btu)

Fuel	Source					
	Battelle 1971 (Reference 2-18)	MSST 1972 (Reference 2-4)	GCA 1973 (Reference 2-15)	Current 1974	Aerospace 1975, projected (Reference 2-17)	NEDS 1976[a]
Coal	2808	1768	1370	3123	1374	1909
Oil	3587	5539	1700	3989	2682	3669
Gas	5729	4182	5200	6371	3520	26244
Process Gas	482	305	—	482	1740	b
Total	12606	11794	8270	13965	9316	31852

[a] Output of National Emissions Data System on August 16, 1976; contains data from 1974 and 1975.

[b] 3.5×10^{12} ft^3 of process gas of unspecified heat content.

TABLE A2-8. ANNUAL NO_X EMISSIONS FROM INDUSTRIAL BOILERS (10^6 tons)[a]

Fuel	Source					
	Battelle 1971 (Reference 2-18)	MSST 1972 (Reference 2-4)	GCA 1973 (Reference 2-15)	Current 1974	Aerospace 1975, projected (Reference 2-17)	NEDS 1976[b]
Coal	0.889	0.515	0.590	0.771	0.592	0.726
Oil	0.727	1.098	0.430	0.843	0.459	0.447
Gas	0.543	0.495	0.420	0.830	0.303	0.788[c]
Total	2.159	2.108	1.440	2.444	1.354	1.961

[a] By convention all NO_x emissions are reported as equivalent NO_2.

[b] Output of National Emissions Data System on August 16, 1976; contains data from 1974 and 1975.

[c] Includes 0.096×10^6 tons due to process gas.

TABLE A2-9. EMISSIONS, EMISSION FACTORS, AND FUEL USAGE FOR COMMERCIAL BOILERS, 1974

Equipment Type	Firing Type	Fuel	Fuel Type	Fuel Usage 10^{12} Btu	Emission Factors lb $NO_2/10^6$ Btu	Total NO_x Emissions 10^6 tons NO_2
Packaged Firetube Scotch	Wall Firing	Oil	Distillate	516.65	0.157	0.0406
			Residual	516.65	0.430	0.1111
		Gas	—	655.41	0.230	0.0750
Packaged Firetube Firebox	Wall Firing	Oil	Distillate	516.65	0.157	0.0406
			Residual	516.65	0.430	0.1111
		Gas	—	655.41	0.230	0.0750
Packaged Firetube Firebox, Stoker	All Categories	Coal	—	165.72	0.417	0.0350
Packaged Firetube HRT	Wall Firing	Oil	Distillate	258.33	0.157	0.0203
			Residual	258.33	0.430	0.0555
		Gas	—	327.71	0.230	0.0380
Packaged Firetube HRT, Stoker	All Categories	Coal	—	82.86	0.417	0.0170
Packaged Firetube, General, Not Classified	Wall Firing	Oil	Distillate	86.91	0.157	0.0068
			Residual	79.91	0.430	0.0172
		Gas	—	109.24	0.103	0.0056
	Stoker and Handfire	Coal	—	18.41	0.25	0.0023
Packaged Cast Iron Boilers	Wall Firing	Oil	Distillate	258.33	0.157	0.0203
			Residual	258.33	0.430	0.0555
		Gas	—	409.63	0.120	0.0250
Packaged Watertube Coil	Wall Firing	Oil	Distillate	28.01	0.157	0.0022
			Residual	34.28	0.430	0.0074
		Gas	—	43.69	0.103	0.0023
Packaged Watertube Firebox	Wall Firing	Oil	Distillate	16.85	0.157	0.0013
			Residual	22.84	0.430	0.0049
		Gas	—	18.21	0.103	0.0009
Packaged Watertube General, Not Classified	Wall Firing	Oil	Distillate	28.01	0.157	0.0022
			Residual	34.28	0.430	0.0074
		Gas	—	43.69	0.103	0.0023

TABLE A2-10. EMISSIONS, EMISSION FACTORS, AND FUEL USAGE FOR RESIDENTIAL SPACE HEATING

Equipment Type	Firing Type	Fuel	Fuel Type	Fuel Usage 10^{12} Btu	Emission Factor lb $NO_2/10^6$ Btu	Total NO_x Emissions 10^6 tons NO_2
Steam or Hot Water Heaters	Single Burner	Oil	Distillate	1207.49	0.128	0.0773
		Gas	–	1000.11	0.082	0.0410
Hot Air Furnaces	Single Burner	Oil	Distillate	1331.93	0.128	0.0852
		Gas	–	2929.80	0.082	0.1201
Floor, Wall, or Pipeless Heaters	Single Burner	Oil	Distillate	199.11	0.128	0.0127
		Gas	–	675.04	0.082	0.0277
Room Heater With Flue	Single Burner	Oil	Distillate	298.67	0.128	0.0191
		Gas	–	700.06	0.082	0.0287
Room Heater Without Flue	Single Burner	Oil	Distillate	190.79	0.082	0.0078

TABLE A2-11. SUMMARY OF ANNUAL NO_x EMISSIONS AND FUEL CONSUMPTION FOR COMMERCIAL AND RESIDENTIAL SPACE HEATING, 1974

Sector	NO_x Emission (Column %) 10^6 tons NO_2				Fuel Consumption (Column %) 10^{12} Btu			
	Oil	Gas	Coal	Total	Oil	Gas	Coal	Total
Commercial	0.5043(71.4)	0.2241(50.8)	0.0543(100)	0.7827(65.1)	3431(51.5)	2263(29.9)	267(100)	5961(41.1)
Residential	0.2021(28.6)	0.2175(49.2)	–	0.4196(34.9)	3228(48.5)	5305(70.1)	–	8533(58.9)
Total	0.7064	0.4416	0.0543	1.2023	6659	7568	267	14494

TABLE A2-12. ANNUAL FUEL USAGE FOR THE COMMERCIAL/RESIDENTIAL SECTOR (10^{12} Btu)

Fuel	Source								
	AP-73 1968 (Ref. 2-25)	AP-115 1969 (Ref. 2-26)	Bureau of Mines 1970 (Ref. 2-27)	MSST 1972 (Ref. 2-4)	FEA 1973 (Ref. 2-28)	GCA 1973 (Ref. 2-14)	Current 1974	FEA 1974 (Ref. 2-28)	FEA 1975 (Ref. 2-28)
Coal	550	406	408	232	295	348	267	297	208
Oil	4152	4182	6440	5960	7077	4659	6659	6688	6340
Gas	6525	6982	7366	7661	7577	7364	7568	7427	7629

TABLE A2-13. ANNUAL NO_X EMISSIONS FROM COMMERCIAL BOILERS (10^6 tons)

Fuel	Source			
	Battelle 1971 (Reference 2-18)	MSST 1972 (Reference 2-4)	GCA 1973 (Reference 2-15)	Current 1974
Coal	0.131	0.029	0.030	0.0543
Oil	0.148	0.212	0.63	0.5044
Gas	0.025	0.120	0.110	0.2241
Total	0.304	0.361	0.77	0.7828

TABLE A2-14. ANNUAL NO_X EMISSIONS FROM RESIDENTIAL SPACE HEATING (10^6 tons)

Fuel	Source			
	Battelle 1971 (Reference 2-18)	MSST 1972 (Reference 2-4)	GCA 1973 (Reference 2-15)	Current 1974
Coal	–	–	0.012	–
Oil	0.1682	0.254	0.098	0.2021
Gas	0.1785	0.212	0.210	0.2175
Total	0.3467	0.466	0.320	0.4196

TABLE A2-15. EMISSIONS, EMISSION FACTORS, AND FUEL USAGE BY EQUIPMENT CATEGORY FOR INTERNAL COMBUSTION ENGINES, 1974

Equipment Type	Firing Type	Fuel	Fuel Usage 10^{12} Btu	Emission Factors, lb $NO_2/10^6$ Btu	Total NO_x Emissions 10^6 tons
Reciprocating Engines	Spark ignition	Gas	1007.73	4.40	2.22
	Diesel >500 hp	Oil	63.76	4.16	0.13
	Diesel <500 hp	Oil	139.30	3.41	0.24
		Dual	51.01	2.91	0.07
Gas turbines		Gas	608.86	0.45	0.14
		Oil	285.64	0.85	0.12

TABLE A2-16. ANNUAL FUEL CONSUMPTION BY INTERNAL COMBUSTION ENGINES 10^{12} (Btu)

Fuel	Source		
	Shell 1971 (Reference 2-29)	MSST 1972 (Reference 2-4)	Current 1974
Oil	477	519	540
Gas	1497	1627	1617

TABLE A2-17. ANNUAL NO_x EMISSIONS FROM INTERNAL COMBUSTION ENGINES (10^6 tons)

Equipment	Fuel	Source		
		Shell 1971 (Reference 2-29)	MSST 1972 (Reference 2-4)	Current 1974
Reciprocating Engines	Oil and Dual	0.40	0.316	0.44
	Gas	1.74	1.871	2.22
Turbines	Oil	0.03	0.119	0.12
	Gas	0.08	0.172	0.14
Total		2.25	2.48	2.92

TABLE A2-18. SUMMARY OF ANNUAL EMISSIONS FOR INDUSTRIAL PROCESS HEATING EQUIPMENT

Industry	Application	Fuel	Current NO_x Estimates for 1974 10^6 tons NO_2	NEDS 1976	IGT (Reference 2-36)
Glass	Melting	Oil	0.0625	0.0091	—
	Furnace	Gas	0.0117		
Petroleum	Catalytic cracker	Oil	0.050	0.0347	—
	Process Heaters	Oil/Gas	0.162	—	—
Cement	Drying kilns	All	0.109	0.131	0.107
Steel and Iron	Coke oven overfire	Gas	0.006	—	0.0297
	Heating annealing ovens	Oil/Gas	0.007	0.0208	0.1290
	Open hearth ovens	—	0.022		0.0533
	Sintering	—	0.029	—	0.0326
Bricks	Curing	Oil/Gas	0.008	0.00225	—
Miscellaneous	Flares	Gas	0.009		—
Total			0.476		

TABLE A2-19. SUMMARY OF ANNUAL NO_X EMISSIONS FROM INCINERATION

Industry	Application	Total NO_x Emissions 10^6 tons
Incineration	Industrial	0.024
	Municipal	0.019
Total		0.043

TABLE A2-20. SUMMARY OF ANNUAL EMISSIONS FOR NONCOMBUSTION SOURCES

Industry	Application	NO_x, 10^6 tons
Acid	Sulfuric	0.012
	Nitric	0.140
	Adipic	0.016
Explosive		0.056
Total		0.224

TABLE A2-21. ESTIMATE OF ANNUAL NO_X EMISSIONS FROM OTHER SOURCES

Source	NO_x 10^3 tons
Solid waste disposal	165
Forest wildfires	152
Prescribed burning	33
Agriculture burning	14
Coal refuse fires	58
Structural fires	7
Misc. (welding, grain silos, etc.)	50
Total	479

TABLE A2-22. SUMMARY OF TOTAL NO_X EMISSIONS FROM FUEL USER SOURCES (1974)[a]

Sector	NO_X Production 10^6 ton/yr (percent of total)			Totals by Sector 10^6 ton/yr (percent of total)	Cumulative Percentage
	Gas	Coal	Oil		
Utility Boilers	0.946 (7.0)	3.840 (28.6)	0.842 (6.3)	5.628 (41.9)	41.9
IC Engines					
Reciprocating	2.220 (16.5)	—	0.440 (3.3)	2.660 (19.8)	61.7
Gas Turbines	0.140 (1.1)	—	0.120 (0.9)	0.260 (2.0)	63.7
Industrial Boilers	0.829 (6.2)	0.768 (5.8)	0.843 (6.3)	2.444 (18.2)	81.9
Commercial/Residential Heating	0.4416 (3.3)	0.0543 (0.4)	0.707 (5.2)	1.2024 (9.0)	90.9
Process Heating	—	—	—	0.476 (3.5)	94.4
Noncombustion	—	—	—	0.224 (1.7)	96.1
Incineration	—	—	—	0.043 (0.3)	96.4
Others	—	—	—	0.479 (3.6)	100.0
TOTALS BY FUEL	4.5766 (34.1)	4.6623 (34.8)	2.952 (22.1)	13.416 (100.0)	

[a] 10^6 tons = 0.909 x 10^6 metric tons

TABLE A2-23. SUMMARY OF ANNUAL FUEL USAGE, 1974

Sector	Fuel Usage[a] — 10^{12} Btu (percentage of total)			Total
	Gas	Coal	Oil	
Utility Boilers	3200 (6.95)	9417 (20.44)	2841 (6.17)	15458 (33.55)
IC Engines				
Reciprocating	1008 (2.19)	—	254 (0.55)	1262 (2.74)
Turbines	608 (1.32)	—	286 (0.62)	894 (1.94)
Industrial Boilers	6853 (14.87)	3123 (6.78)	3989 (8.66)	13965 (30.31)
Commercial Boilers	2263 (4.91)	267 (0.58)	3431 (7.45)	5961 (12.94)
Residential Heating	5305 (11.51)	—	3228 (7.01)	8533 (18.52)
TOTAL	19237 (41.75	12807 (27.80)	14029 (30.45)	46073 (100.0)

[a] Excludes process fuel.

TABLE A2-24. COMPARISONS OF ANNUAL NO_X EMISSIONS DATA

Sector	10^6 tons (NO_2)					
	ESSO (1968)	AP-115 (1970)	OAQPS (1971)	MSST (1972)	GCA (1973)	Current (1974)
Utility Boilers	3.84	4.71	5.38	5.67	6.50	5.628
IC Engines				(2.48)		
Reciprocating	2.10[b]	d	d	2.19	1.64	2.660
Gas Turbines	a	d	d	0.29	0.491	0.260
Industrial Boilers	2.81	4.53	3.90	2.11	1.44	2.444
Commercial	1.00	0.23	0.586	0.36	0.77	0.783
Residential	1.00	0.57	0.586	0.47	0.32	0.420
Process Heating	a	0.20	a	0.39	—	0.476
Noncombustion	0.24	—	0.20	0.149	—	0.224
Incineration	a	0.08	0.04	0.04	0.017	0.043
Other	c	c		c		0.479
TOTAL	10.99	10.32	10.69	11.67	11.18	13.416

[a] Included in industrial size boilers.
[b] Pipeline and gas plants only.
[c] Not included in data.
[d] Included in utility and industrial depending on use.

TABLE A2-25. ANNUAL FUEL CONSUMPTION COMPARISONS

Sector	10^{15} Btu				
	OAQPS (1971)	AP-115 (1969)	MSST (1972)	GCA (1973)	Current (1974)
Utility Boilers	14.04	12.14	14.78	14.80	15.41
IC Engines					
Reciprocating	—	—	1.26	2.01	1.26
Gas Turbine	—	—	0.89	1.34	0.89
Industrial Boilers	16.86[a]	16.11[a]	11.79	8.27	13.97
Commercial	12.20	11.57	4.13	4.45	5.96
Residential			9.71	7.92	8.53
TOTAL	43.10	39.82	42.56	38.79	46.08

[a] Includes IC engines

TABLE A2-26. ANNUAL NATIONWIDE NO_X EMISSIONS PROJECTED TO 2000
(Reference 2-37)

Source Category	NO_x Emissions (10^6 tons)				
	1972	1980	1985	1990	2000
Stationary Fuel Combustion	12.27	15.96	16.82	18.46	21.74
		(17.12)[a]	(21.43)	(27.14)	(44.46)
Electric Generation	5.94	8.16	8.20	8.88	10.24
		(9.32)	(12.81)	(17.56)	(32.96)
Industrial	5.39	6.73	7.46	8.31	10.01
Commercial-Institutional	0.65	0.76	0.84	0.93	1.11
Residential	0.29	0.31	0.32	0.34	0.38
Industrial Process Losses[b]	0.70	0.95	1.14	1.38	1.85
Solid Waste Disposal	0.18	0.22	0.25	0.28	0.34
Miscellaneous	0.59	0.74	0.87	1.02	1.32
TOTAL	13.74	17.87	19.08	21.14	25.25
		(19.03)	(23.69)	(29.82)	(47.97)

[a] NO_x emissions for no new nuclear power plants after 1975 are given in parentheses.

[b] Industrial process losses corrected for 1972 reporting error in Reference 2-36.

TABLE A2-27. ESTIMATED FUTURE NSPS CONTROLS
(Reference 2-38)

NO$_x$ Source		Date Implemented	Standard (lb/10^6 Btu)
Utility and Large Industrial Boilers (<73 MW)[a]	Coal	1971	0.7
		1977	0.6
		1981	0.5
		1985	0.4
		1988	0.3
	Oil	1971	0.3
	Gas	1971	0.2
Large Packaged Boilers (<7.3 MW)[a]	Coal	1979	0.6
		1985	0.5
		1990	0.4
	Oil	1979	0.2
	Gas	1979	0.3
Small Packaged Boilers (>7.3 MW)[a]	Coal	1979	50% reduction
	Oil	1979	0.2
	Gas	1979	0.3
Small Commercial and Residential Units			
	Oil	1983	0.07
	Gas	1983	0.04
Gas Turbines		1977	0.3
		1983	0.2
IC Engines	Dist Oil	1972	3.2
		1985	2.4
	Nat Gas	1979	2.9
		1985	2.1
	Gasoline	1979	2.2
		1985	1.6
Process Combustion		1981	20% reduction
		1990	40% reduction

[a] Thermal input

TABLE A2-28. ANNUAL NATIONWIDE NO_X EMISSION TO 2000 (Reference 2-38)

Source Category	NO_x Emissions (10^6 tons)				
	1974	Low Nuclear		High Nuclear	
		1985	2000	1985	2000
Electric Generation	6.137	8.170	11.140	7.078	6.644
Packaged Boilers	2.585	2.571	1.815	2.252	2.047
Internal Combustion	2.532	1.796	1.465	1.796	1.465
Warm Air Heating	0.354	0.288	0.267	0.288	0.267
Industrial Process	0.476	0.287	0.331	0.287	0.331
Incineration	0.044	0.058	0.084	0.058	0.084
Noncombustion	0.213	0.264	0.355	0.264	0.355
TOTAL	12.341	13.434	15.457	12.023	11.193

TABLE A4-13. EFFECTS OF NO_x CONTROLS ON PARTICULATE EMISSIONS FROM COAL-FIRED UTILITY BOILERS (References 4-12,4-16)

Firing Mode	Particulate Emissions ($lb/10^6$ Btu)		% Carbon on Particulate	
	Baseline	Low NO_x	Baseline	Low NO_x
Front-Wall	4.65 - 7.89	3.84 - 5.62	5.90 - 6.29	8.46 - 12.4
Horizontally Opposed	3.03 - 3.84	3.12 - 4.14	2.8 - 5.5	6.73 - 11.82
	7.65 - 8.91	5.59 - 8.38	0.53 - 0.69	0.18 - 0.46
Tangential	2.00 - 5.14	5.49 - 5.57	24.2 - 25.8	14.8 - 18.8
	2.50 - 4.27	2.87 - 6.85	0.92 - 1.98	0.8 - 1.53

TABLE A4-29. REPRESENTATIVE EFFECTS OF NO_x CONTROLS ON CO EMISSIONS FROM INTERNAL COMBUSTION ENGINES (Reference 4-56)

Fuel	Engine Type	Baseline Emissions (lb/10^6 Btu)	NO_x Control CO Emissions (lb/10^6 Btu)					
			Derate	Retard Ignition	Increase A/F	Decrease A/F	Reduce MAT	Water Injection
Natural Gas	2-cycle	0.065 - 0.093	0.092 - 0.217	0.084 - 0.105	0.067 - 0.071	--	0.068 - 0.105	--
	4-cycle	0.175 - 7.8	0.126 - 0.346	0.187 - 2.34	--[a]	0.272	0.304	0.45
Diesel	2-cycle	0.168 - 0.755	0.208	0.326 - 1.46	--	--	0.166	1.08
	4-cycle	0.265 - 1.27	0.24 - 0.42	0.604 - 1.52	1.02	1.57	0.33 - 1.28	1.07 - 1.41
Dual Fuel	2-cycle	0.384	0.568	0.568 - 0.62	--	0.568	0.156	--
	4-cycle	0.465 - 1.56	0.672	1.58 - 2.48	0.67	0.689	1.47	1.17 - 1.18

[a] denotes no data reported.

TABLE A6-4. CAPITAL AND OPERATING COSTS FOR DIFFERENT NO_x ABATEMENT SYSTEMS IN A 300 TPD NITRIC ACID PLANT (Reference 6-6 and 6-26)

	Catalyst Reduction	Molecular Sieve	Grande Paroisse	CDL/ Vitok	Masar	Goodpasture
Capital Investment,[a] ($)	1,384,000	1,200,000	1,000,000	575,000	663,000	425,000
Royalty	--	--	included	none	fee	51,000
Operating Labor, (hr/yr)	360	360	360	360	360	360
($/yr)	2,200	2,200	2,200	2,200	2,200	2,200
Maintenance Labor,	315	315	315	315	540	315
($/yr)	2,200	2,200	2,200	2,200	3,775	2,200
Labor Overhead (incl. fringe	4,400	4,400	4,400	4,400	5,975	4,400
benefits & supervision, $/yr)						--
Catalyst or Molecular Sieve	77,800	45,600	--	--	--	30
Cooling Water, (gpm)	--	500	300	1,020	--	440
($/yr)	--	7,330	4,420	14,980	--	--
Steam, (lb/yr)	(15,833)[c]	250	--	715	1,310	--
($/yr credit)	(387,590)	6,120	--	17,500	32,070	45
Electricity, (kW)	128	322	90	265	20	7340
($/yr)	20,890	52,550	14,690	43,250	3,260	--
Boiler Feed Water, (gpm)	35	--	--	--	--	--
($/yr)	12,850	--	--	--	--	--
Fuel, (10^6 Btu/hr)	28.5	2.0	--	--	--	--
($/yr)	465,120	32,640	--	--	--	--
Nitric Acid, (tpd)	--	(6.6)	(6.0)	(6.0)	(5.28)	--
($/yr)	--	(112,200)	(102,000)	(102,000)	(89,760)	--
Urea, tpd					1.37[b]	--
($/yr)					74,528	--
Ammonium Nitrate, (tpd)					1.25	(13.0)
($/yr)					(42,500)	(422,000)
Depreciation (11-yr life)	125,900	109,090	90,910	52,300	60,300	38,640
Return on Investment (@ 20%)	276,800	240,000	200,000	115,000	132,600	85,000
Taxes & Insurance, (@ 2%)	27,700	24,000	20,000	11,500	13,260	8,500
Total Annual Cost, ($/yr)	628,270	413,930	236,780	161,330	195,708	(42,290)
Annual Cost, ($/ton)	6.16	4.06	2.32	1.58	1.92	(0.42)

[a] Investment estimates exclude interest during construction, owners expenses, and land costs.

[b] Includes credit for 0.0017 tons of urea/ton or nitric acid produced present in the spent solution (D.SITPD).

[c] Parenthesis indicate credit taken.

TABLE A6-5. ANNUAL ENERGY REQUIREMENTS (10^9 Btu) FOR NO_X ABATEMENT SYSTEMS FOR A 300 TPD NITRIC ACID PLANT (Reference 6-6 and 6-26)

	Basic Nitric Acid Plant	Catalytic Reduction	Molecular Sieve	Grande Paroisse	CDL/ Vitok	Masar	Goodpasture
Steam (Credit)	(71.4)	(129.20)	2.04	-	5.83	10.69	-
Electrical	-	10.97	27.59	7.71	22.71	1.71	1.38
Natural Gas	163.2	232.56	-	-	-	-	-
Oil	-	-	16.32	-	-	-	-
	91.8	114.33	45.95	7.71	28.54	12.40	1.38

TABLE A6-6. BASIS FOR TABLES A6-4 AND A6-5 (Reference 6-6)

(Plant Capacity @ 300 tpd and 102,000 tons/yr)

(March 1975 Dollars, ENR Index = 2.126)

1.	Operating Labor	@ \$6.1/hr
2.	Maintenance Labor	@ \$7.0/hr
3.	Overhead	@ 100% of labor (including fringe benefits and supervision)
4.	Cooling Water	@ \$0.03 1,000 gal
5.	Boiler Feedwater	@ \$0.75 1,000 gal
6.	Natural Gas	@ \$2.00/10^6 Btu
7.	Oil	@ \$2.00/10^6 Btu
8.	Depreciation	@ 11 yr straight line
9.	Return on Investment	@ 20% of capital cost
10.	Taxes and Insurance	@ 2% of capital cost
11.	Nitric Acid	@ \$90/ton
12.	Urea	@ \$160/ton
13.	Ammonium Nitrate	@ \$100/ton
14.	1 kWh = 10,500 Btu	
15.	Electricity	@ \$0.02/kWh
16.	Ammonia	@ \$157/ton

APPENDIX B

PREFIXES FOR SI UNITS

The names of multiples and submultiples of SI units may be formed by application of these prefixes:

Factor by Which Unit is Multiplied	Prefix	Symbol
10^{18}	exa	E
10^{15}	peta	P
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{2}	hecto	h
10	deka	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a

APPENDIX C

GLOSSARY

Biased Firing — An off-stoichiometric combustion technique in which the burners of a wall-fired utility boiler are operated either fuel- or air-rich in a staggered configuration.

Boiler Efficiency — $\frac{\text{Heat Output}}{\text{Heat Input}} \times 100.$

The overall figure reflects combustion efficiency, radiation and convection losses from the boiler, and heat lost in exhaust gases.

Burners Out Of Service (BOOS) — An off-stoichiometric combustion technique in which some burners are operated on air only.

Combustion Modification — An alteration of the normal burner/firebox configuration or operation employed for the purpose of reducing the formation of nitrogen oxides.

Derating — Reducing the heat input and power or steam output of a boiler below the level for which it was designed.

Excess Air — Any increment of air greater than the stoichiometric fuel requirement. With gas-, oil-, and coal-fired boilers, some excess air is used to assure optimum combustion.

Field-Erected Boiler — All components of a boiler are delivered to the site and assembled in the field. Mainly pertains to utility and large industrial boilers.

Firetube Boiler — Steam or hot water generator with heat transfer surface consisting of steel tubes surrounded by water and carrying hot combustion gases.

Flue Gas Recirculation (FGR) — A combustion modification in which a portion of the boiler exhaust gases are recirculated to the burners to inhibit NO formation.

Flue Gas Treatment — A process which treats tail gases chemically to remove NO_x before release to the atmosphere.

Fuel Nitrogen — Nitrogen that is chemically bound in the fuel.

Heat Input — The product of the fuel feedrate and the higher heating value, e.g., 10 Mg per hour of coal with a higher heating value of 29 MJ/kg provides a heat input of 80.5 MW (290GJ/h).

Heat Release Rate — The rate of combustion per unit volume of firebox, typically in terms of MW/m^3.

Higher or Gross Heating Value (HHV) — The heat generated by complete combustion of a fuel, always referenced to baseline temperature, e.g., 16°C. Heat available at the reference temperature is included in the higher heating value even if it is not practically available, i.e., heat of condensing water vapor.

Low Excess Air — A combustion modification in which NO_x formation is inhibited by reducing the excess air to less than normal ratios.

Lower or Net Heating Value (LHV) — The heat that is practically available from a fuel to generate steam or otherwise raise the temperature of the media receiving energy. The net heating value assumes complete combustion. It differs from the higher heating value in that heat of vaporizing water of combustion is considered a recoverable loss.

Off-Stoichiometric Combustion (OSC) — A combustion modification technique in which burner stoichiometry is altered to inhibit NO_x formation. Types of OSC include biased firing, burners out of service, and two-stage combustion.

Packaged Boilers — These are usually boilers that are smaller and more economically assembled at the plant, then shipped to the boiler site as one integral unit ready for operation after connection to water, stream, and power.

Polycyclic Organic Matter (POM) — Organic compounds which exists in condensed phase at ambient temperature and are emitted as either "carbon on particulate" or condensed onto emitted particulate.

Polynuclear Aromatic Hydrocarbons (PNA) — Same as POM.

Stoichiometric Air — That quantity of air which supplies only enough oxygen to react with the combustible portion of the fuel.

Two-Stage Combustion — A type of off-stoichiometric combustion in which the burners are operated fuel-rich and the remainder of the required combustion air is introduced through separate ducts located above the burner. This is also called "overfire air" or "NO_x port operation.

Watertube Boiler — A steam generator with heat transfer surface consisting of steel tubes carrying water that are exposed to hot combustion gases.